



## Demineralization of low grade coal – A review



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### ABSTRACT

World over large reserves of low grade coals are available. The use of low-grade coal in various industries like power plants, metallurgical plants, cement units, etc. creates environmental pollution because of generation of large amount of solid and gaseous pollutants. Therefore, it is of paramount importance to clean the coal before its utilization. A number of upgrading technologies are being followed to produce clean coal. The current paper reviews demineralization/desulfurization of coals containing high ash and/or sulfur by physical, microwave, bio- and chemical beneficiation methods. Physical beneficiation of coal is not very effective in separation of the finely dispersed minerals, whereas microwave processing requires lesser time but is not favoured energetically. Bio-processing is mainly used for the desulfurization of high sulfur coal, although it is usually slow and requires long incubation period. Chemical beneficiation uses expensive reagents and leads to the generation of large amount of wastewater which is to be purified before discharge. Thus, a combined approach consisting of physical beneficiation followed by chemical cleaning of coal appears to have a potential for significant reduction of ash with less investment while generating less amount of wastewater.

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## 1. Introduction

Coal is the single largest fossil energy source used world-wide and is possibly the largest contributor to the industrial growth [1]. Coal plays a key role in electricity generation and is input to most iron and steel production, and cement units. As estimated by the World Coal Association, 70% of the world's steel production is based on coal and 41% of the world electricity generation is through coal [2]. The full utilization of coal as a resource has been limited by the presence of high levels of ash and sulfur in its major deposits. Because of the world energy crisis, rising price of crude oil and natural gas, and gradual depletion of high-quality coal reserves of the world, demineralization and/or desulfurization of low-grade coals to obtain environmentally acceptable clean fuels has attracted greater attention. Considering the limited reserves of petroleum and natural gas, eco-conversion restriction on hydro-electric projects and geo-political perception of nuclear power, coal will continue to occupy the center stage of global energy scenario [3]. Particularly in India about 55% of the current total commercial energy is met by coal and more than 75% of non-coking coal is used for power generation [4].

### 1.1. Coal formation

Coal goes through several changes during formation. Coal forms in swampy areas as a result of the decay of plants in the absence of oxygen. Biochemical changes produced by bacteria release oxygen, hydrogen and hence carbon content is concentrated. Coal beds consist of altered plant remains. When forested swamps die, they sink below the water and begin the process of coal formation. In swamp where coal forms, other sediments such as sand, clay and silt may also deposit. The weight of the sediment compresses the underlying organic matter. Due to the increase in pressure with time, impurities and moisture are squeezed out leaving a high carbon concentration.

There are four stages of formation of coal: peat, lignite, bituminous and anthracite. These stages depend upon the conditions under which the plant remains were subjected after they were buried – greater the pressure and heat, higher the rank of coal. Higher-ranking coal is denser and contains less moisture and gases, and has a higher heat value than lower-ranking coal (Table 1).

Peat, the first stage of formation of coal, contains a lot of water and has a fibrous, soft and spongy texture. The water content must be dried before its use as a source of heat/energy and it burns with a long flame and smoke, therefore it is generally not advised for industrial purposes. Subsequent burial of the peat results in the decrease of water content. This process normally extinguishes bacterial activity, and as temperature rises with increasing depth of burial the coalification processes begin to transform the peat to brown coal, then lignite, sub-bituminous and bituminous coal, and finally to anthracite. Lignite is dark brown in color and contains traces of plants. It is used only if no other source of fuel is available. Bituminous coal also known as soft coal with no remains of plant material is used greatly in industries as a source of fuel. Anthracite or hard coal is the final stage in coal formation and is formed due to high temperature and pressure. This type of coal has the texture of a rock and has some luster. It produces small flame and little smoke.

Coal may be classified into scientific and commercial category relating the ultimate and proximate analysis, respectively. Out of the classification suggested by International Organization for

standardization (ISO), ASTM and British Standard Institution (BSI), the most accepted one is by ASTM which is based on the proximate analysis to designate the rank and grade of coal [9].

### 1.2. Coking and non-coking coals

Coking coals are used for production of coke which is used in steel industries and non-coking coals are required for thermal power plants for steam production. Coking coals are hard porous substance that comprises about 90% carbon with the balance being ash (non-combustible material), volatile matter and other impurities such as sulfur and phosphorus. When coking coal is heated in absence of air, it leaves a solid coherent residue possessing metallic greyish luster and has the physical and chemical properties of the coke. The non-coking coals also leave solid coherent residue, but may not be suitable for manufacture of coke. This coal may form a coke but it will not meet the physical and chemical properties as laid down by the steel industry. It can be used in the reduction of metallic oxides to metals.

Coking coals are those coals that soften, swell and then solidify as they are heated through the temperature range 350–550 °C. By definition these coals all have a low ash content (1–10%), low permeability as determined by inherent moisture, moderate vitrinite content (to provide volatile matter) and volatile matter in the range 18–45%. The reflectance of the maceral vitrinite is also used as a measure of coals suitability for coking. Reflectance measures the amount of light that is reflected from a polished piece of vitrinite and for coking coals it is in the range 0.6–1.8% (range of bituminous coals). The coals with the lowest reflectance have the lowest rank and the highest volatile matter.

**Table 1**  
Stages in coal formation and their properties [5].

Coalification stage	Moisture <sup>a</sup> (%)	Volatile matter <sup>b</sup> (%)	Carbon content <sup>b</sup> (%)	Calorific value <sup>a</sup> (kcal/kg)	Oxygen content <sup>b</sup> (%)
Peat	~75	69–63	< 60	3500	> 23
Lignite	35–55	63–53	65–70	4000–4200	23
Sub-bituminous C	30–38	53–50	70–72	4200–4600	20
Sub-bituminous B	25–30	50–46	72–74	4600–5000	18
Sub-bituminous A	18–25	46–42	74–76	5000–5500	16
High volatile bituminous C	12–18	46–42	76–78	5500–5900	12
High volatile bituminous B	10–12	42–38	78–80	5900–6300	10
High volatile bituminous A	8–10	38–31	80–82	6300–7000	8
Medium volatile bituminous	8–10	31–22	82–86	7000–8000	4
Low volatile	8–10	22–14	86–90	8000–8600	3
Semi-Anthracite	8–10	14–8	90	7800–8000	3.5
Anthracite	7–9	8–3	92	7600–7800	4.5
Meta-Anthracite	7–9	8–3	> 92	7600	5

<sup>a</sup> As received basis.

<sup>b</sup> Dry ash free basis.

**Table 2**  
Requirements of coal quality for various plants / industries [6].

Characteristics	Metallurgical grade	Sponge iron plant	Thermal power plant	Cement industries [IS 12770:1989]
Moisture	Max. 10%	6%	Max. 8–12%	Max. 8%
Volatile matter	20–35%	Min. 30%	Min. 19%	Min. 24%
Ash	Should be ~10%	22–25%	Max. 34%	Max. 24–27%
Sulfur	Max. 0.6%	Max. 1.0%	Max. 0.8%	Max. 0.8%
Size, mm	–	–25+3	Max. 250	Max. 250

At present all coking coals are processed in India to meet the specification of steel sector with a cut-off grade of 16–17% ash content. The middlings of the process is sent to the power plant. Apart from being used as an energy source for generating electricity, coal is also used in various other industries and manufacturing plants for the production of coke, cement, paper, syngas (synthetic gas) and chemicals. Coal is also used as a house hold fuel. The coal quality requirements for various plants/industries are given in Table 2.

### 1.3. Mineral matters in coal

Coal generally incorporates various amounts of mineral matter as impurity. The presence of mineral matter adversely affects most aspects of coal utilization and processing. Mineral matter is the inert solid material in the coal which remains behind in a slightly altered form as ash after coal combustion. The mineral matter finds its way into the peat bed during the formation of the coal (syngenetic) and can be included during mining in terms of roof and floor inclusions. Table 3 summarizes the minerals commonly occurring in coals. Mineral matter can be divided into either inherent or extraneous mineral matter. Liberated minerals which are not attached or included in the organic component are classified as adventitious or excluded, whereas minerals that are surrounded by or included in an organic matrix, are classified as inherent or included minerals. Clays, quartz, carbonate and pyrite group of minerals are examples of inherent mineral matter. Extraneous mineral matter occurs as partings and lenses in the coal seam as well as shale, sandstones and intermediate rocks introduced during the mining of the coal bed. In addition to the above, pyrite, ankerite and calcite can exist in the form of extraneous mineral matters which are deposited in the coal seam after its formation.

Ash is generally well intermixed into the coal structure and hence coal washing using physical methods can remove it to a limited extent, although it might be necessary for some industrial application. The high ash content also leads to technical difficulties for utilizing the coal, and is coupled with lower efficiency and higher costs of power plants. Some specific problems with high ash content in coal include high ash disposal requirements, corrosion of boiler walls, fouling of economizers and high fly ash emissions [8]. Some disadvantages of the use of coal as fuel with respect to gas and liquid fossil fuels are due to the slagging and fouling in the combustion chamber, and to the emissions of toxic particulate matter, trace metals and SO<sub>2</sub>.

**Macerals:** Macerals are the fragmentary organic remains of plants that died. Due to exposure to the heat and partial decay in the crust of the earth through time they are altered to peat, and are subsequently converted to the final state in the coal. The carbonaceous/combustible fraction of coal is made up of macerals which consist of more than half of the coal mass.

Maceral content of coal is measured by the reflected light method. When direct light is applied to the polished coal surface each maceral reflects characteristic amounts of light. It is generally granted that the

**Table 3**  
Mineral matters in coal [7].

Mineral	Group	Mineral idealized formula
Clay	Kaolinite	Al <sub>2</sub> SiO <sub>5</sub> (OH) <sub>4</sub>
	Muscovite	KAl <sub>2</sub> (Si <sub>3</sub> Al)O <sub>10</sub> (OH) <sub>2</sub>
	Illite	K <sub>1–1.5</sub> Al <sub>4</sub> [Si <sub>6–7</sub> Al <sub>1–1.5</sub> O <sub>20</sub> ](OH) <sub>4</sub>
	Smectite	(Na,Ca·nH <sub>2</sub> O)(Al <sub>2</sub> Mg <sub>y</sub> )(OH) <sub>2</sub> (Si <sub>2x</sub> Al <sub>x</sub> )O <sub>10</sub>
Oxides	Quartz	SiO <sub>2</sub>
	Rutile	TiO <sub>2</sub>
	Anatase	
Carbonates	Calcite	CaCO <sub>3</sub>
	Aragonite	
	Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>
	Ankerite	Ca(FeMg)CO <sub>3</sub>
	Siderite	FeCO <sub>3</sub>
	Rhodochrosite	MnCO <sub>3</sub>
Feldspars	Orthoclase	KAlSi <sub>3</sub> O <sub>8</sub>
	Microcline	
	Plagioclase	Na[AlSi <sub>3</sub> O <sub>8</sub> ]-Ca[Al <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> ]
Scapolite	Analcime	NaAlSi <sub>3</sub> O <sub>6</sub> ·H <sub>2</sub> O
Sulfides	Pyrite	FeS <sub>2</sub>
	Marcasite	
Phosphates	Apatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (F, Cl, OH)
	Crandallite	CaAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>5</sub> ·H <sub>2</sub> O
	Gorceixite	BaAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>5</sub> ·H <sub>2</sub> O
	Goyazite	SrAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>5</sub> ·H <sub>2</sub> O
Sulfates	Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O
	Alunite	KAl <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
	Jarosite	KFe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>

reflectance of the macerals increases with the increasing rank of the coal, but there has been some controversy as to whether the increase occurs in a series of sudden jumps at certain ranks, or is a continuous change process. Reflectance measurements are an objective method to classify the petrographic constituents of the coal.

Transmitted-light technique is another method of determining the petrographic composition of coal. The transmitted light technique has not been as widely adopted as the reflected-light technique, possibly because of the difficulties encountered in performing the required thin-section preparation and analysis.

The groups of macerals in coals are vitrinite, inertinite, exinite (liptinite), etc. Vitrinite macerals are in the humic fraction of coal wall substances. A woody texture and brown color characterize vitrinites in coals of early metamorphic stages. Bituminous low-rank vitrinites show color from buff and cream to yellow, tan and pale orange red; in vertically incident light, they appear gray and have less than 5% reflectance. Vitrinite of intermediate rank are tan, orange red, reddish brown, and deep red, and they reflect 0.5–2.5% of vertically incident light. High-rank vitrinites in anthracites are opaque and have a reflectance of 2.5–6%.

Inertinite (Fusinite) macerals are from the charcoal like fraction of coal and are produced by rapid charring and alteration of all wall material. They appear white in vertical incident light and opaque in thin section. Exinite (liptinite) macerals are derived from waxy secretions such as plant cuticles and spore, and pollen exines. In very high rank coals, they have the same optical properties as vitrinite or they disappear. In low to intermediate rank coals, they are yellow in thin section and dark gray to black in the medium range.

The best coke forming maceral is vitrinite. It is relatively inert in anthracite and it will neither cake nor soften in the low-rank and high volatile coals. But, if the volatile matter content of the coal is from ~19% to 33%, vitrinite is responsible for the actual coking properties. Coking coals usually have characteristic contents of vitrinite, inertinite and exinite [10].

**Table 4**  
Proven recoverable coal reserves (in million tons) [11].

Country	Anthracite and Bituminous	Sub-bituminous	Lignite	Total	% of the World
United States	108,501	98,618	30,176	237,295	22.6
Russia	49,088	97,472	10,450	157,010	14.4
China	62,200	33,700	18,600	114,500	12.6
Australia	37,100	2100	37,200	76,400	8.9
India	56,100	0	4500	60,600	7.0
Germany	99	0	40,600	40,699	4.7
Ukraine	15,351	16,577	1945	33,873	3.9
Kazakhstan	21,500	0	12,100	33,600	3.9
South Africa	30,156	0	0	30,156	3.5
Serbia	9	361	13,400	13,770	1.6
Colombia	6366	380	0	6746	0.8
Canada	3474	872	2236	6528	0.8
Poland	4338	0	1371	5709	0.7
Indonesia	1520	2904	1105	5529	0.6
Brazil	0	4559	0	4559	0.5
Greece	0	0	3020	3020	0.4
Bosnia and Herzegovina	484	0	2369	2853	0.3
Mongolia	1170	0	1350	2520	0.3
Bulgaria	2	190	2174	2366	0.3
Pakistan	0	166	1904	2070	0.3
Turkey	529	0	1814	2343	0.3
Uzbekistan	47	0	1853	1900	0.2
Hungary	13	439	1208	1660	0.2
Thailand	0	0	1239	1239	0.1
Mexico	860	300	51	1211	0.1
Iran	1203	0	0	1203	0.1
Czech Republic	192	0	908	1100	0.1
Kyrgyzstan	0	0	812	812	0.1
Albania	0	0	794	794	0.1
North Korea	300	300	0	600	0.1
New Zealand	33	205	333–7000	571–15,000	0.1
Spain	200	300	30	530	0.1
Laos	4	0	499	503	0.1
Zimbabwe	502	0	0	502	0.1
Argentina	0	0	500	500	0.1
All others	3421	1346	846	5613	0.7
World total	404,762	260,789	195,387	860,938	100

#### 1.4. Global coal scenario

Globally, coal resources have been estimated at over 861 billion tons (BT) [11]. Of the three fossil fuels, coal has the most widely distributed reserves and is mined in over 100 countries. The largest reserves are found in the United States, Russia, China, Australia and India [Table 4]. China, which is only number four in reported reserves, is by far the top producer, almost twice as big as the USA which has twice as much reported deposits. As reported by Geological Survey of India (GSI), Central Mine Planning and Design Institute Limited (CMPDI) and other agencies, India has 286 BT coal resources as on 2011. Out of these resources, 114 BT are proven, 137 BT as indicated reserves and the remaining over 34 BT are in inferred category. Of the total resources, prime-coking coal is 5 BT, medium-coking and semi-coking 28 BT and non-coking coal 252 BT, which includes coal with high sulfur.

Gondwana coalfields, which are mainly in the eastern and central parts of India, have primarily concentrated coal deposits. In Assam, Arunachal Pradesh, Nagaland and Meghalaya tertiary coal sediments are found. There were 559 coal mines (till 2011) in India. Out of which, in Jharkhand 174 mines were located, West Bengal had 98 mines, Madhya Pradesh 71, Chhattisgarh 62, Maharashtra 55, Andhra Pradesh 50 and Odisha had 28 mines. The remaining 21 mines were located in the states of Arunachal Pradesh, Assam, Jammu & Kashmir, Meghalaya and Uttar Pradesh [12].

State/coalfield wise and type wise reserves of coal as on 2011 are given in Tables 5 and 6 respectively.

**Table 5**  
Indian coal reserves in different states/coalfield as on 2011 (million tons) [13].

State/coalfield	Proven	Indicated	Inferred	Total
<b>Gondwana coalfields</b>	<b>113,407.79</b>	<b>137,371.76</b>	<b>33,590.02</b>	<b>284,369.57</b>
Andhra Pradesh	9296.85	9728.37	3029.36	22,054.58
Assam	–	2.79	–	2.79
Bihar	–	–	160.00	160.00
Chhattisgarh	12,878.99	32,390.38	4010.88	49,280.25
Jharkhand	39,760.73	32,591.56	6583.69	78,935.98
Madhya Pradesh	8871.31	12,191.72	2062.70	23,125.73
Maharashtra	5489.61	3094.29	1949.51	10,533.41
Odisha	24,491.71	33,986.96	10,680.21	69,158.88
Sikkim	–	58.25	42.98	101.23
Uttar Pradesh	866.05	195.75	–	1061.80
West Bengal	11,752.54	13,131.69	5070.69	29,954.92
<b>Tertiary coalfields</b>	<b>593.81</b>	<b>99.34</b>	<b>799.49</b>	<b>1492.64</b>
Assam	464.78	42.72	3.02	510.52
Arunachal Pradesh	31.23	40.11	18.89	90.23
Meghalaya	89.04	16.51	470.93	576.48
Nagaland	8.76	–	306.65	315.41
<b>All India: total</b>	<b>114,001.60</b>	<b>137,471.10</b>	<b>34,389.51</b>	<b>285,862.21</b>

**Table 6**  
Reserves of Indian coal types (million tons) as on 2011 [13].

Type of coal	Proven	Indicated	Inferred	Total
Prime coking	4614.35	698.71	–	5313.06
Medium coking	12,572.52	1,200.132	1880.23	26,454.07
Semi-coking	482.16	1003.29	221.68	1707.13
Non-coking	95,738.76	123,668.44	31,488.11	250,895.31
High sulfur	593.81	99.34	799.49	1492.64
All India: total	114,001.60	137,471.10	34,389.51	285,862.21

#### 1.5. Characteristics of Indian coals

Indian coals are primarily bituminous and sub-bituminous type. Run-of-mine coals typically have high ash content (ranging from 30% to 50%), high moisture content (4–20%), low sulfur content (0.2–0.7%) and low calorific values (between 2500 and 5000 kcal/kg) [13]. In the north-east region of the country, sulfur content in the coal is very high (2–5%), although such coals have relatively better coking properties and lower ash contents (5–10%). The quality of these coals is poor in comparison to that of other countries due to high sulfur content. The mineralogical analysis of Indian coals shows the presence of mineral matter in the form of kaolinite, silica (quartz, opal, cherts) and clay. The high sulfur and ash content restricts large scale utilization of several Indian coals.

Because of the poor quality of Indian coals due to high ash content, it is difficult to clean them as the ash-forming minerals being finely disseminated in the coal matrices. Much of the coals burned for power generation (thermal power plant) are generally raw coals containing 35–50% ash. Besides silica and clay minerals, coal also contains various carbonates, sulfates, sulfides, oxides, etc. The major constituents of ash in Indian coals are silica ( $\text{SiO}_2$ ), alumina ( $\text{Al}_2\text{O}_3$ ) and iron oxide ( $\text{Fe}_2\text{O}_3$ ). Despite this, it has a number of favorable properties such as (i) low sulfur ( $< 1\%$ ) and phosphorous content ( $< 0.2\%$ ), (ii) high ash fusion temperature ( $> 1500^\circ\text{C}$ ), (iii) low iron content in the ash, (iv) low chlorine content, (v) low toxic/rare elements, (vi) refractory nature of the ash, and (vii) macerals (inertinite and liptinite) rich combustion friendly coal.

In India, coal from the surface/open cast mines is commonly of lower quality than those from the underground mines due to non-selective inclusion of inter-burden. Most Indian coals have high mineral matter varying from 15% to greater than 50%. Since the washability characteristics of these coals are poor, it is difficult to remove the mineral matter by conventional techniques based on the above principles for coke making and power generation [14].



Washing of thermal coal in India is typically carried out to target less than 34% ash. Ministry of Environment and Forest promulgated (2001) new regulations mandating that coals must be cleaned to less than 34% ash content if transported for > 1000 km from pitheads, or if burned in urban areas, environmentally sensitive or critically polluted areas irrespective of their distance from the pit-head [15]. The coals consumed at the pithead and within a rail distance of 1000 km can be burned without washing. The use of such coals for any application creates several problems and requires preparation and cleaning before utilization.

### 1.6. Demineralization/desulfurization of coals

The mineral matters associated with the coal are of two types – one is chemically bonded with organic matter and the other exists as separate entity. Demineralization and desulfurization of coal may be achieved by both physical and chemical methods.

The high silica and alumina content in coal is a problem, as it increases ash resistivity which reduces the collection efficiency of electrostatic precipitators, and increases emissions. Coal beneficiation may be the solution to the above problems that can –

1. produce higher quality coals with high calorific value and increase coal utilization efficiency,
2. reduce the amounts of emitted fly ash and associated hazardous air pollutant precursors,
3. minimize capital, operating and maintenance costs of boilers in thermal power plants,
4. minimize transportation and storage cost,
5. reduce the need to import high quality coals; and
6. improve health and safety by mitigating environmental degradation.

Two key principles are applied to separate higher grade coal material (higher calorific value and lower ash content) from lower grade carbonaceous material, and other mineral matter under physical beneficiation. These principles are reflected in

- (i) Processes based on differences in relative density (RD) between coal and associated mineral matter. Pure coal has an RD of  $\sim 1.3$  and shale contamination has an RD of  $> 2.2$ .
- (ii) Processes based on differences in surface properties between coal and associated mineral.

The desulfurization of coal prior to combustion is reported either by physical, biological or chemical methods. Coal is hydrophobic and associated mineral matter is generally hydrophilic. Physical methods are only capable of removing large pyritic particles. Such processes are cost effective, but may not be effective in separating the finely dispersed minerals and those bound to the coal structure. The biological techniques, however, are time-consuming with some of the microbes specifically removing only certain types of sulfur forms. Most of the effective coal desulfurization techniques are based on chemical methods whereby almost all the pyritic sulfur, ash and substantial amount of organic sulfur can be removed from the coal. The chemical methods for the demineralization of coal have some advantages because both types of mineral species can be leached out.

Demineralization of coal can be achieved by using acidic or basic agents. Basic solutions, such as NaOH, KOH,  $\text{Ca(OH)}_2$ , or acidic solutions such as HF, HCl,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , as well as  $\text{H}_2\text{O}_2$  and combinations of all these chemicals have been attempted to remove the undesired minerals [16]. Besides methods like physical, biological and chemical, solvent extraction, thermal, nuclear, oxidation, electrochemical, alkali and hydrosulfurization are also reported for demineralization and desulfurization of the coals

[17–30]. The effectiveness of these methods depends on the type of coal and the sulfur content. Much research has been carried out on desulfurization/demineralization via chemical methods [23,26,29]. The reagent type must be selected with the aim of an effective desulfurization and demineralization.

## 2. Physical beneficiation of coal

Physical beneficiation techniques as mentioned earlier may be broadly classified as those based on specific gravity and surface properties of the mineral and carbonaceous parts. Processes based on surface properties (wettability) are froth flotation, flotation by Jameson cell, column flotation, oleo flotation and oil agglomeration, whereas difference in density properties is utilized in jigs, shaking tables, spirals, cyclone and dense medium separation. In almost all the gravity based techniques, it has been noted that a classification step prior to beneficiation is essential for effective treatment. Magnetic susceptibility of the gangue/impurities is employed in magnetic separation and electrostatic separation utilizes the difference in conductivity or dielectric properties.

The role of coal cleaning for the removal of toxic elements has been discussed by Akers and Dospoy [31] in greater depth. Coal cleaning as a means of abating emission of potential trace elements offers the advantages of relatively low cost, improved boiler thermal efficiency and reduction of  $\text{SO}_2$  emissions. However, cleaning based on physical beneficiation is unlikely to provide complete removal of the rare and trace elements. Physical treatment particularly flotation, magnetic separation or the use of hydrocyclones mainly removes inorganic sulfur, whereas elimination of organic sulfur requires in most cases chemical and/or microbial treatment [32]. Some of the processes/techniques for deashing and desulfurization of coal are discussed in brief.

### 2.1. Gravity separation techniques

Gravity separation, which is governed by the differences in specific gravity between coal and mineral matters (ash-forming minerals and pyrite), is widely used in the coal preparation. Among gravity separation techniques, dense medium separation is one of the most prevalent processes. Other gravity separation techniques include centrifuge, jig, landers, etc. Despite its efficiency in ash removal for relatively coarse coal, they are not so useful in fine coal cleaning. In fact the gravity beneficiation for coal usually requires feed size larger than 0.5 mm. Sulfur mineral viz., pyrite is usually finely disseminated in coal matrix and can be liberated only by grinding to a finer size, thus cannot be removed by gravity separation.

The development of an enhanced gravity concentrator such as Mozley Multi-Gravity Separator (MGS), which is successful to concentrate cassiterite, chromite, etc., shows promise in fine coal treatment. Gravity based separator for coal cleaning employs a dense-medium which comprises of an aqueous suspension of ultrafine magnetite. The density of the suspension is adjusted in between the densities of coal and the associated mineral matter, so that the light coal particles float while the heavy particles (mineral matter) sink. To achieve an efficient separation an enhanced gravity field is required, which can be achieved using small diameter cyclones ( $\sim 15$ – $20$  cm) and/or by high feed pressures ( $> 690$  kPa). Gravity based processes are much more efficient than flotation for treatment of middling particles. Enhanced density separators [31] such as the Mosley Multi-Gravity Separator and the Falcon and Knelson concentrators are used for the processing of coal fines of size  $< 0.25$  mm. These types of separators are mechanically-driven devices that produce large dynamic force to enhance a density separation, using high-gravity forces coupled with flowing-film or tabling techniques to effect the

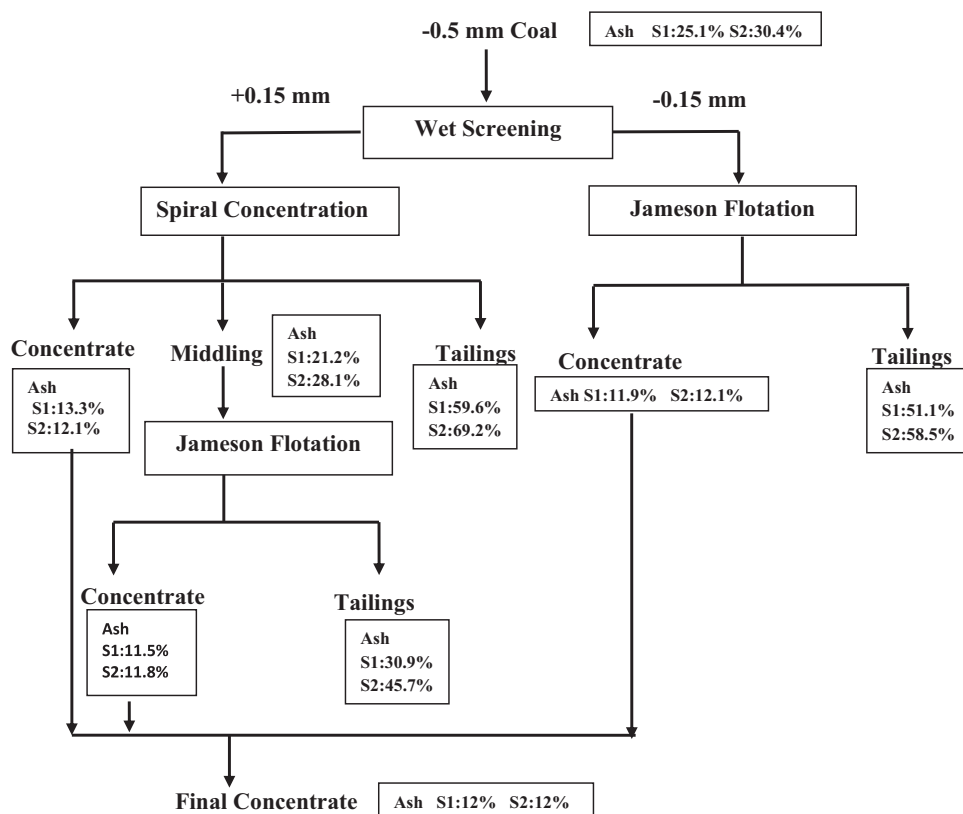


Fig. 1. Modified flow diagram developed for the split processing of the two coals [39]. (S1 and S2: sample nos. 1 and 2).

separation. The application of high-pressure feed injection into the dense-medium cyclones to provide an elevated centrifugal force has been found to allow efficient separation performance for the treatment of fine coal (i.e. < 1000  $\mu\text{m}$ ) [34]. Results showed that the process reduced the ash content of a difficult-to-clean coal from 29% to nearly 7%.

The beneficiation of two lignite tailings containing 66% and 53% ash, by Multi-Gravity Separator (MGS) was investigated by Özgen et al. [35]. It was possible to produce cleaner coals containing ~23% ash with a recovery of 49.3% and 60.01%. An enhanced gravity separator (Falcon concentrator) was used for the concentration of fine and ultra-fine minerals [36]. It was shown that the Falcon concentrator can produce a clean coal with an ash value of 36% from a feed coal of about 66% ash with a recovery of about 35%. Similarly, Honaker et al. [37] obtained the ash rejection values between 60% and 70% from the treatment of several fine coal samples using Falcon concentrator with a recovery of greater than 85% of the combustibles. In another study Honaker et al. [33] showed high ash and total sulfur rejections from a semi-continuous Falcon concentrator with a recovery of more than 90% of the coal.

Recently, Rath et al. [38] concluded that Falcon concentrator was not able to reduce the ash content to low values as compared to the froth flotation. The maximum ash reduction of 47.5% was achieved from that of 60% with a yield of 35% by using Falcon concentrator while froth flotation showed better result with 34% ash at a yield of 23%. A combination of gravity separation and Jameson cell separation process for cleaning fine coal that does not exhibit good floatability has been demonstrated by Das et al. [39]. They have shown that if the floatability was poor or moderate, then split processing (a combination of spiral concentration of the coarser fraction and froth flotation of the finer fraction using a Jameson cell) improved coal cleaning performance. The split processing flow

diagram for Indian coals named as S1 and S3 with different ash contents is shown in Fig. 1 [39].

## 2.2. Froth flotation

Froth flotation is separation of minerals that differ greatly in wettability by using a surface active agent which can stabilize a froth formed on the surface of an agitated suspension of the substance in water. Primarily, the ash and sulfur-bearing minerals found in coal are hydrophilic, and therefore should remain in the tailings during the process of flotation. Generally, froth flotation is the technique used for the beneficiation of coal particles below 0.5 mm in size. Froth flotation has been used to recover fine coal (< 0.6 mm) for over 50 years. The carbonaceous mineral constituents of coal being hydrophilic in nature, can be made to preferentially attach to fine bubbles and float to the surface of a dilute slurry, where they can be removed, while in contrast the low carbonaceous inert minerals of the raw coal do not attach to the bubbles [40].

The air introduced into the flotation cells is stabilized as froth by a frothing reagent such as pine oil or kerosene. Selectivity of the process can be improved by the addition of surfactant chemicals (collectors) to selectively increase the hydrophobicity of the carbonaceous particles. However, efficiency of the process depends on the hydrophobicity of the particles and even small portion of coal matter in the gangue would be a great loss [41]. Again flotation reagent cost adds up to the processing cost which makes the flotation method more expensive than other physical methods. Yet, to remove inorganic materials viz. pyritic sulfur, the most suitable process is flotation to clean coal provided it is liberated in feed [42].

The conventional froth flotation process operates in approximately equi-dimensional open cells with a mechanical system to agitate the

slurry in a turbulent flow of bubbles, commonly referred to as mechanical flotation. A more recent technical development, which has become common in the last 10 years, is column flotation, which uses the same principle of separation but takes place in columnar vessels without mechanical agitation.

There are now many types of column flotation cells commercially available with several more under development. Individual columns of up to 7 m diameter with feed capacities of up to 80 tph are now in use. Technical variations range from simple columns where air or an air/water mixture is injected at the base e.g. the pyramid system [43] to more complex systems. In the microcel system [44], slurry is recirculated through the sparging system to create shearing forces. In the Jameson cell [45], the particles and bubbles are attached in a down-coming feed tube. Other systems such as, the turbo-column [46] present a hybrid of the conventional cells with a number of innovative features. In this technique, the particles to be floated coat the carrier material and the coated particles are then floated. Carrier flotation for desulfurization and deashing of difficult-to-float coals was reported by Atesok et al. [47]. Under the optimum conditions, a fine ( $-38\ \mu\text{m}$ ) concentrate containing 8.3% ash and 0.72% total sulfur with a recovery of 81% was obtained from a feed containing 16.3% ash and 2.0% total sulfur. The addition of pitch was found to further improve the performance of carrier-flotation.

Flotation characteristics of oxidized Indian high ash sub-bituminous coal from Talcher coal field, India were studied by Jena et al. [48]. Initially the flotation study was carried out using conventional reagents only in a Denver D-12 sub-aeration flotation cell. Then it was pre-treated with aliphatic alcohols i.e., ethanol and butanol to de-oxidize the coal surface. The beneficiated coal with 31% ash content and 80.4% yield was produced from a coal containing 41–42% ash. In case of column flotation, ash could be reduced further to 26.6% from the same coal with 66.5% yield.

The effect of pH, collector (kerosene) amount and frother type (MIBC, AF 76, pine oil, DF 250) for depressing pyrite from the Hazro coal was investigated by Ayhan et al. [49]. The best flotation conditions were found to be: pH 9, kerosene 250 g/t, and methyl isobutyl carbinol (MIBC) as the frother. By the flotation method  $\sim 50\%$  ash content was reduced along with the removal of most of sulfate sulfur ( $> 90\%$ ) and 67% of the pyritic sulfur from the coal sample. Column flotation has an advantage over conventional flotation as it can provide higher concentrate grade and recovery, lower maintenance costs, and improved process control [50].

Flotation variables are the pH of pulp, types and dosages of reagents, percentage of solid in pulp, temperature and agitation rate [51]. Reagent used and type of the reagent are important factors in froth flotation. The effect of reagents and reagent mixtures on flotation of bituminous coal fines (23.95% ash) was investigated [52]. The highest recoveries ( $> 90\%$ ) were achieved in the presence of conventional reagents like MIBC or sodium dodecyl sulfate (SDS). However, ash rejection values were lower with the same reagents which were considerably improved by using the mixture of reagents.

Reduction of ash and sulfur from Tabas coal, Iran by flotation was studied by Reza and Farahnaz [53]. Use of kerosene and methanol as collectors decreased the ash and sulfur content of the coal by 40–50% and 30%, respectively, but kerosene at 125 g/t consumption yielded more recovery of coal ( $\sim 80\%$ ) than the methanol.

The floatability and liberation characteristics of hard-to-float high-ash coal slime sample from China and its potential separation processes were investigated by Xiu-xiang et al. [54]. Experimental results indicated that classified flotation could not effectively improve the fine coal quality, while the processes of fine grinding–recleaning to roughing cleaning coal and selective agglomeration–flotation were suitable for this coal. Compared with the original coal

flotation process, the processes of fine grinding–recleaning to roughing cleaning of coal increased the cumulative yield from 50.8% up to 55.5% while reducing the product ash content from 11.8% to 10.7%. In the selective agglomeration–flotation process, the lowest ash level in clean coal is found to be 10.7% with 58.7% yield, 7.8% higher in yield and 1.1% lower in ash content.

Conventional flotation circuits are generally inefficient in recovering fine coals. As a result the rejects of flotation plant still contain considerable coal values which can be recovered by using more efficient equipments like flotation column [55,56]. Investigations were carried out using column flotation to recover coking coal fines from the tailings generated at flotation plant of one of the operating washeries in India [57]. Investigation on tailings of flotation plant indicated that the rejects had got the potential to yield 60% clean coal with 15% ash level.

### 2.3. Oil agglomeration

Among the physical methods, the oil agglomeration process [58] has drawn special attention in recent years. The process of agglomeration is based on the principle that coal particles are naturally hydrophobic or at least less hydrophilic than inorganic materials, and can therefore, be agglomerated and separated from the mineral matter by the addition of a suitable bridging liquid that wets the carbonaceous constituents.

The oil agglomeration process is very promising for

- Beneficiation of coal, especially for the extreme fines which cannot be treated by conventional processes.
- Recovery and upgrading of coal slurries and effluents originating from the conventional coal preparation plants, and
- Preparation of coal that has specifically low ash and inorganic sulfur contents.

A physical method of cleaning Assam coal from India by agglomeration with xylene and hexane was reported by Baruah et al. [59]. The maximum organic matter recovery for xylene has been found to be 92% whereas with hexane the value is about 55% on a dry basis. The highest ash rejection values with xylene and hexane are almost the same (90%).

Various vegetable oils (both edible and non-edible) were tested in order to find out their efficiency as agglomerants with respect to five widely different Indian coking and thermal coals [60]. It was observed that the yield of agglomerates ranged from 40.0% to 87.5% and ash rejections from 13.5% to 62.0% using different coal–oil combinations. Bacterial pre-treatment of coal with mixed culture prior to oil agglomeration improved the selectivity of vegetable oils resulting in higher ash rejections (59–76%). Also, pre-treatment of high sulfur coal with *Acidithiobacillus ferrooxidans* culture resulted in significant enhancement in pyritic sulfur rejection from 69% to 98.5%. Spherical oil agglomeration of bituminous coal fines was carried out using diesel oil as a bridging liquid [61].

Surface based separation processes such as flotation and oil agglomeration have been traditionally recognized as the practical methods for cleaning fine coal. These processes are very selective in rejecting well liberated mineral matter, but are much less effective if the feed coal contains a disproportionate amount of composite particles. Pyrite cannot be floated if the surface chemistry of the flotation pulp is not properly controlled.

### 2.4. Magnetic separation

An important and promising physical method for the possible removal of ash and sulfur from coal is the magnetic separation technique based on difference in the natural magnetic properties of the coal and associated mineral impurities. Coal is a weak diamagnetic

material. A particle gets magnetized to some extent in the presence of magnetic field and acts as a magnetic dipole. Magnetic separation may be used for coal beneficiation when the gangue minerals contain iron phase. The magnetic susceptibilities are very small for coal separations and therefore, strong magnetic field is required. Some of the iron containing minerals in coal is strongly paramagnetic and the sulfur bearing and major ash forming minerals in coals are also paramagnetic; hence they can normally be separated from remaining diamagnetic matters by magnetic means [62]. Significant level of ash reduction can be achieved by magnetic separation in this case. Magnetic separation of coal material can be accomplished by two methods namely High-Gradient Magnetic Separation (HGMS) and Open-Gradient Magnetic Separation (OGMS). With the former, the separation is achieved by applying a large force over a short distance, while in the latter, a smaller force is applied over a much larger distance.

Depending upon the types of coals used and the separation conditions employed, the existing bench-scale and pilot scale results have shown that the use of single-pass HGMS was effective in reducing the total sulfur by 40%, the ash by 35% and the pyritic sulfur by 80%. A maximum coal recovery of about 95% was achieved in the process [63].

Wet and dry methods have been used in high-gradient magnetic separation for the desulfurization of pulverized coal. The dry methods may be desirable because they require the lowest initial capital investment and have the lowest maintenance costs of all currently used methods of upgrading fine coal. Gravity-enhanced high-gradient magnetic separation has been successfully applied for the removal of mineral impurities from coal with a 4-T superconducting solenoid magnet [64]. Under optimum separation conditions, this technique effectively cleaned up to 72% of the pyritic sulfur and 44% of the ash content from a typical pulverized coal in a vertically upward airstream rig, with the heating value recovery of almost 95%.

A combination of semi-coking followed by a permanent roll magnetic separator (PERM ROLL) has been used for upgrading a Turkish low-rank lignitic coal [65]. Initially coal sample was carbonized at 600 °C and was then subjected to PERM ROLL. Under the optimum conditions, carbonization of lignite particles in  $-9+0.5$  mm size range which contained 12.2% ash and 3.4% total sulfur produced a product containing 25.9% ash and 3.2% total sulfur (on a dry basis). After that dry magnetic separation employing the PERM ROLL upgraded this product to 11.2% ash and 1.4% total sulfur with a recovery of 31.5% based on the feed to the carbonization process.

## 2.5. Electro-static separation

As an advanced dry fine coal cleaning technology, the triboelectrostatic beneficiation can effectively process the fine coal of less than 74  $\mu\text{m}$  size. Triboelectrostatic separation of the associated minerals from coal is based on the difference of work function and the conductance of minerals and coal. Separation occurs under the influence of very high electric field. Prior to the separation stage, particles have to be electro-statically charged. The separation of a mineral from the organic phase in the coal is based on the difference in the ability of the two phases to develop and maintain charges in different types of separators. Two such types of electrostatic processes are in vogue, one uses the difference in electric resistivity while the other uses difference in the electronic surface structure [66,67]. Conductive induction, tribo-electrification and Ion or Corona bombardment are common commercial methods of electric separation. Coal is generally less conducting than the mineral matter, except perhaps in the case of brown coal which has high water content and also often has high ion content [68]. Pyrite is the most conducting mineral that is commonly found in the coal.

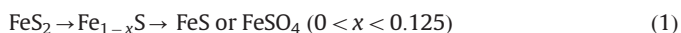
There are two mechanisms for particle charging: corona charging and triboelectric charging mechanism. In corona charging mechanism, all particles are charged but lose the charge at different rates depending upon their conductivity, and are separated based on the difference in remaining charge. In triboelectric charging (friction or contact), clean coal generally charges positively and ash forming minerals charge negatively to make the separation [68–70]. Tribo-electric separations of coal and associated tribo-charging characteristics have been investigated by many researchers for successful separation of the mineral matter from coal [71–77].

Inculet et al. [78] had successfully beneficiated the coal to remove ash while retaining calorific value by the dry electrostatic separation process using a fluidized bed for triboelectrification. Recovery and ash contents of the beneficiated coal were comparable to the recoveries by water washing. The triboelectrostatic method was applied to beneficiate non-coking Indian thermal coal containing 43% ash. Tests on a laboratory in-house built triboelectrostatic free-fall separator with  $< 300 \mu\text{m}$  coal showed that the ash content was reduced from 43% to about 18%, and a clean coal product as judged by the washability studies can be obtained [79]. Research on the triboelectrostatic separation of minerals from coal was also carried out by Zhang et al. [80]. The quartz, kaolin and pyrite can be removed effectively by triboelectrostatic separation from coal. Results showed that the kaolin and pyrite were easier to remove than quartz.

A comparison of various physical beneficiation processes for coal is presented in Table 7.

## 2.6. Microwave processing

The treatment of coal by microwave irradiation [frequency 2.45 GHz/wavelength 12.2 cm and energy  $1.22 \times 10^{-5}$  eV for most industrial applications] depends on its dielectric properties [81–83]. The difference in dielectric characteristics of organic and inorganic matters in the coal results in differential heating with microwave [84]. Chatterjee et al. [85] determined the dielectric constant of dry coal, pyrite and mineral matter (without pyrite) to be 3, 7 and 4.6, respectively. The high energy density of the microwave can be used to heat quickly for minimal heat loss to the coal, with the pyritic phase absorbing more energy than the rest of the coal matrix [81,86]. The magnetic susceptibility of pyrite also improves on heating due to the conversion of  $\text{FeS}_2$  to  $\text{FeS}$ , a strongly magnetic material [87]. The conversion of pyrite to pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ) after microwave treatment (Eq. (1)) was confirmed [88–90], which increased the magnetic susceptibility of coal and making it easier to desulfurize using magnetic separation.



The inorganic sulfur removal was found to be 44% at the irradiation time of 100 s. On combining the process with HCl (5%) washing which attacked pyrrhotite by forming  $\text{H}_2\text{S}$ , a 97% decrease in inorganic sulfur was obtained [88]. Microwave is reported to break the bonds of S–Fe in pyrite and S–C in organic sulfur with the release of some sulfur in gaseous form; the conversion being 10% and more in some cases [91]. This technique shows significant liberation of iron and sulfide phases in the coal [89]. In a similar experiment Uslu and Atalay [92] heated coal with magnetite addition under microwave for 300 s before magnetic separation and mineralogical analysis. The magnetite was essential for increasing the medium temperature to sufficiently heat the pyrite. Thus pyritic sulfur was found to decrease by 55.1% and ash by 21.5%, while the calorific value increased by 20.4%, compared to the decrease of 22.3% pyrite and 15.8% ash in the conventional stove-top heating.



**Table 7**

A comparison of various physical beneficiation processes for coal.

Technique	Principle	Feed size	Advantages	Disadvantages	Ref.
Gravity separation	Difference in specific gravity of coal and mineral matters (ash-forming minerals and pyrite)	> 0.5 mm	Most efficient for removing undesirable gangue materials from ROM coal and also for treatment of middlings.	Sulfur minerals are usually finely disseminated in coal matrix and can be liberated only by grinding to a finer size.	[31]
Froth flotation	Difference in surface properties and hydrophobicity of coal and other minerals is driving force to separate pyrite and ash forming minerals.	< 0.5 mm	Relatively low capital and space requirements, as well as relatively high recovery achievable under a wide range of operating conditions.	Using large quantity of water and loss of millions of tons of coal in tailing ponds.	[40]
Oil agglomeration	Difference in the surface properties of organic and inorganic particles.	Extreme fines (< 75 $\mu\text{m}$ )	Able to minimize fine coal losses and to recover combustible matter from refuse ponds.	Pyrite is readily wetted by fuel oil and agglomerated due to its weakly hydrophobic surface compared to other minerals (hydrophilic). Oil makes the process costly.	[61]
Magnetic separation	Difference in natural magnetic properties of coal and associated mineral impurities.	< 125 $\mu\text{m}$ (for dry magnetic separation).	Insensitivity to coal chemistry makes it useful for oxidized coals and magnetic separation is able to remove locked coal/pyrite.	Magnetic susceptibility – very small for coal separations and needs strong magnetic field.	[62]
Electro-static separation	Difference in dielectric property of coal and minerals to maintain/dissipate an induced charge under dynamic conditions.	< 74 $\mu\text{m}$	Electrostatic forces work on particles to be separated only; they do not affect the medium in which particles are located.	Limitation of maximum mass that it can effectively work upon. Continuous power supply is also needed for separation.	[66]

Microwave processing is thus an emerging technique used for ore and coal beneficiation [90–93]. The principal advantage of microwave treatment is the energy and time reduction, while lowering the costs in the minerals processing industry [94]. In terms of desulfurization of coal using microwave energy as discussed above, the selective heating property of the minerals can be exploited to free them from the coal matrix.

Chemical desulfurization of low rank coal using HI (acid) as a desulfurizing agent with microwaves as the energy source was investigated by Andrés et al. [95]. The experiment involved exposing the coal and hydriodic acid mixture to microwaves in an inert argon atmosphere. After 10 min of exposure time, approximately 99% of the pyritic sulfur was removed and an organic sulfur removal of 65% was achieved after 20 min of irradiation. In a similar study by Yürüm et al. [96] the chemically treated pulverized coal (–65 mm) sample was treated in microwave for 20 min in an inert atmosphere. This method removed all the pyritic sulfur and 70% of the organic sulfur, but the process was not cost effective [96].

The effect of molten caustics in coal desulfurisation using microwave energy was reported by Hayashi et al. [97]. Easy removal of pyritic sulfur by alternate means such as wet washing or magnetic separation was reported, but it was almost impossible to remove the organic sulfur other than with the molten caustic methods. Jorjani et al. [98] desulfurized coal using a combination of microwave irradiation and peroxyacetic acid. Microwave irradiation was carried out on a pulverized sample for 50, 80, and 110 s at the powers of 600, 800 and 1000 W. The sample was then treated with peroxyacetic acid. This was performed by heating the coal in glacial acetic acid to the required temperature and then adding  $\text{H}_2\text{O}_2$ . Microwave desulfurization alone removed 19% of the sulfur. The peroxyacetic acid washing increased the sulfur removal to 36% after

exposing to microwave for 30 min. Sulfur removal increased with an increase in the residence time.

## 2.7. Dry fluidization

Presently, cleaning of the majority of run-of-mine coal is conducted by heavy media separator, jigs, chemical flotation, etc. In these techniques water is used as a separation medium. It is hardly an advantage to reduce the ash content of a coal by cleaning it and simultaneously water is consumed as product moisture and tailings disposal. Waste generated from wet process after recycling of the water is unsuitable for disposal to water resources, because it contains large amount of waste solids fines, which causes the pollution of water bodies. Problems related to treatment and storage of process waste water can be avoided by using dry processes. Dry process may also result in higher calorific value of the coal. Dry fluidization could be the substitute to the present wet chemical flotation method, whenever fine crushing is needed to liberate the product from gangue.

The fluidized bed provides the difference in the densities of the materials to be separated. So the less dense particles will float on the top of the bed and the heavier ones will sink through it. Mainly, fluidized bed separators can be classified as the following three main types:

1. The Yancey and Frazer separator: The process using this separator is simple and deals with a feed size of 1–5 cm. It separates off coal and refuse by fluidized sand, with a bulk density of 1.45  $\text{g/cm}^3$ . Coal floats across the containing vessel and refuse sinks through the fluidized sand mixture due to its higher density.

- Two separators developed by Warren Spring Laboratories (an inclined bed separator and a sluice box): The inclined bed separator consists of an inclined vibrating trough with a porous base filled with dry sand. Feed sized between 7.5 cm and 0.6 mm can be treated effectively. Here mixtures are added to the sand, thereby excess sand with floating particles overflows the separator at the weir side end. The sinking particles are transported from the bottom to the other end of the incline by vibration. The second separator is the sluice box or Dry Flow separator. This separator consists of an inclined rectangular trough through which dry sand flows. The mixture is added to the sand and stratifies in a heavy and light fraction, then the fractions are separated by using splitter or knife.
- The rectangular trough separator and the circular trough separator: It is used for the sorting of minerals, agricultural products and separation of non-ferrous metal scrap. It consists of a horizontal vibrating trench with circular design that provides the sand circulation, and the sorted material during passage on inclined screens is de-sanded [99].

### 2.8. Limitations of physical beneficiation

Ash is generally well intermixed into the coal structure and hence coal washing using physical methods is difficult, although it might be simple and necessary for industrial use. Some of the limitations of physical coal cleaning are given here:

- Very fine grinding is required to liberate the fine pyrite inclusions. Fine grinding is most energy intensive operation and ultrafine particles are difficult to handle and dewater.
- Desulfurization increases with grinding to finer size but decreases density of the separating medium, leading to the problem of dewatering.
- Only pyritic sulfur can be removed with physical beneficiation and pyrite removal causes certain loss in combustible matter.
- Gravity beneficiation for coal usually requires feed size larger than 0.5 mm.
- Physical separation is not suitable for chemically bound minerals.

Therefore, chemical beneficiation of coal is considered necessary for effective removal of mineral matters which are finely distributed and bound strongly to the coal. It is possible to produce ultra-clean coal (UCC) by reducing ash forming minerals, pyritic sulfur and organic sulfur. Chemical cleaning of coal is simple when it operates under mild conditions. Although chemical processing can usually achieve better impurity removal in comparison to physical processing, higher cost limits its commercial application.

### 3. Bio-processing of coal

Bio-processing of coal is an emerging technology which has been explored with two aims: (i) coal cleaning–removal of sulfur, nitrogen and trace metals by mild microbial processes, and (ii) coal conversion–microbial liquification, microbial gasification, methane production, etc. Bio-processing of coal usually requires lower capital and operating costs; both pyritic and organic sulfur can be removed by microbial catalysis without causing any significant energy loss or coal refuse. This process operates at low temperature (25–75 °C) and atmospheric pressure and therefore, is less energy intensive than the chemical processes. Bio-desulfurization of coal can be achieved by the microbial treatment under laboratory conditions and can be translated to commercial operations.

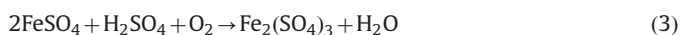
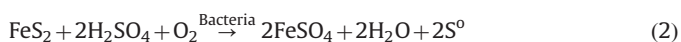
The effect of some filamentous fungi such as *Aspergillus niger* and *Penicillium sp.* on demineralization of low rank (sub-bituminous) coal was studied by Manoj and Elcey [100]. Result showed that the ash content was decreased by about 73% when leached with acclimatized mixed culture of *Aspergillus niger* and *Penicillium sp.* The coal so processed showed an increase of 26.5% in calorific value and that of carbon content by about 20%.

Several microorganisms have been reported for the desulfurization of coals [101,102]. Zarubina et al. [103] and Silverman et al. [101] carried out the biodesulfurization using chemoautotrophic, acidophilic bacteria, *Acidithiobacillus ferrooxidans* and reported the bacterial oxidation of the pyritic sulfur in coal. The bacterium was used as pure and mixed cultures in which other species, such as *A. thiooxidans*, *Leptospirillum ferrooxidans*, *Acidithiobacillus acidophilus*, etc., were present in smaller proportions [102,104]. The advantage of using mixed cultures is to utilize the characteristics of each microorganism.

*A. ferrooxidans* (a sulfur and iron oxidizer) and *L. ferrooxidans* (an iron oxidizer) are capable of oxidizing pyrite when growing in pure culture, whereas *A. thiooxidans* (a sulfur oxidizer) is not able to oxidize pyrite alone, but grows on the sulfur released after the iron is oxidized [103]. *A. thiooxidans* is thought to favor the activity of *A. ferrooxidans* by oxidizing the elemental sulfur formed in intermediate reactions. *A. acidophilus* is known as a satellite microorganism, since in mixed cultures it feeds on the degradation products of *A. ferrooxidans* and *A. thiooxidans* preventing the saturation of the reaction medium by these products [105–107]. Kargi and Robinson [108] used the thermophilic organism, *Sulfolobus acidocaldarius* for the removal of ~44% of initial organic sulfur from 10% coal slurries at 70 °C in about 4 weeks time.

Two types of mechanisms have been suggested for pyrite oxidation, direct and indirect mechanisms. In the direct mechanism, the pyrite is oxidized biologically and it requires physical contact between the bacterium (*Acidithiobacillus ferrooxidans*) and pyrite particles. It is a heterogeneous process in which the bacterial cell attaches itself to the sulfide crystal surface and the corrosion occurs in a thin film located in the interspace between the bacterial outer membrane and the sulfide surface. In the indirect mechanism pyrite slowly oxidizes on exposure to air and water to produce acid and ferrous ion.

Direct mechanism:



In the indirect mechanism ferric ions oxidize the ferrous ions of pyrite leaving  $\text{Fe}^{2+}$  and elemental sulfur.



The elemental sulfur is oxidized by *A. ferrooxidans* to sulfate.



The formation of iron precipitates, mainly jarosites ( $\text{MFe}_3(\text{SO}_4)_2(\text{OH})_6$ ), where M stands for either hydronium, potassium, sodium or ammonium, is a problem in the oxidation of pyrite. The isolation and characterization of *Rhodococcus erythropolis* IGTS8 (formerly called *Rhodococcus rhodochrous* IGTS8) led to major advancements in the investigations of bio-desulfurization of dibenzothiophene present in coal.

Thermophilic microorganisms such as *Sulfolobus acidocaldarius* and *Acidianus brierleyi*, formerly known as *Sulfolobus brierleyi*, were shown to remove pyrite from coal at 70 °C [109]. Both the direct and indirect mechanisms of pyrite oxidation act simultaneously and together. The essential conditions for the oxidation reactions to occur are that the pyrite surface should be accessible

and for this reason, the porosity of the coal plays an important role [110].

Microbial desulfurization of coal has advantages such as a higher pyrite removal efficiency and lower coal wastage than with physical methods, and the reduced cost compared to the chemical methods because microbial methods operate at ambient conditions with the fewer reagents. It is a low energy process operating at atmospheric pressure and low temperature, and can enable sulfur to be separated without loss of coal [111].

Although the above methods were proven to be successful in removing finely disseminated pyrite from coal which is difficult to achieve using physical methods, but the depyritisation process was found to be too slow. Besides it is costly as well, as further dewatering and drying need to be employed before such a coal can be used in industry. The bio-processing of coal by using microbes is an attractive process but its suitability has to be established at the large or pilot scale. Since bio-desulfurization takes a longer duration of about 1–2 weeks, so, further research is essential to reduce the incubation time.

#### 4. Chemical beneficiation of coal

Due to low demineralization achieved by physical techniques to produce clean and ultra-clean coal (UCC), chemical processes are frequently considered. The general approach followed for upgrading the low grade coal involves leaching under a variety of conditions. Chemical cleaning of coal with alkali and acid solutions has proved effective in reducing significant amounts of ash-forming minerals, pyritic sulfur and organic sulfur (disulfides, thiols, sulfides, thiophenes and thioketones) from coal. Chemical demineralization processes, either alone or following physical cleaning processes, have been extensively explored for the production of UCC. Some of the chemical demineralization processes which have been investigated, include leaching with NaOH [112], NaOH followed by mineral acids [113–117], KOH-acids [115,118],  $\text{Na}_2\text{CO}_3$  [119],  $\text{Ca}(\text{OH})_2$  followed by acid washing [120], mineral acids viz.  $\text{HNO}_3$  [121–123],  $\text{HCl}$  [116],  $\text{H}_2\text{SO}_4$  [124,125], oxidizing agents viz.  $\text{H}_2\text{O}_2$  [23,125],  $\text{Fe}_2(\text{SO}_4)_3$  [126],  $\text{K}_2\text{Cr}_2\text{O}_7$  [127],  $\text{NaOCl}$  [128],  $\text{HF}$  [129],  $\text{HF}$  then  $\text{HNO}_3$  [29,130] and sequential leaching by  $\text{NaOH-H}_2\text{SO}_4$  [131].

##### 4.1. Acid leaching

Direct acid leaching is a powerful method to demineralize coals, as summarized in Table 8 [131–138]. A few compounds are dissolved in caustics, but low pH is generally favorable for metal ion solubilization.

Concentrated hydroiodic acid (HI) was used to remove sulfate and pyritic sulfur in Spanish coals at temperatures up to 260 °C and pressures up to 60 bar in a microwave heating setup [132]. Inorganic sulfur was completely removed in the first 10 min of the treatment while 70% of the organic sulfur could be removed only after 20 min. Use of other acids showed low yields.

Hydrofluoric acid (HF) can effectively dissolve quartz and kaolinite. Quartz is more difficult to mobilize than kaolinite, therefore, coal demineralization rate strongly depends on the proportion of quartz and kaolinite in a coal [139].

Fig. 2 shows the two-stage leaching process: HF acid leaching followed by  $\text{HNO}_3/\text{Fe}(\text{NO}_3)_3$  leaching of different bituminous coals. Steel and Patrick [130] investigated the production of UCC by chemical demineralization of a high-volatile British coal containing 7.9% ash and 2.6% sulfur by leaching with HF followed by  $\text{HNO}_3$  solutions. Upon treatment for 3 h at 65 °C, HF reduced the ash content to ~2.6% and the subsequent treatment with  $\text{HNO}_3$  reduced the ash content to 0.63% by dissolving fluoride compounds

formed during HF leaching and iron as  $\text{FeS}_2$ . The remaining ash consists largely of unreacted  $\text{FeS}_2$  encapsulated in the coal structure. This investigation clearly shows that  $\text{HNO}_3$  reacts with  $\text{FeS}_2$  above a particular  $\text{HNO}_3$  concentration and is consumed preferentially to a certain extent with the organic coal structure. The final sulfur content after treatment with HF and  $\text{HNO}_3$  was found to be 1.4%. In a separate study [25] ash content was reduced from 5% to 0.2% and sulfur from 2.4% to 1.3% in a sequential leaching with HF and  $\text{HNO}_3$ .

Producing ultra-clean coal by microwave pre-treatment and sequential leaching with HF and  $\text{HNO}_3$  was reported [140]. The demineralization of bituminous coal of UK using a two-stage leaching by hydrofluoric acid and ferric nitrate [137] showed decrease in ash content from 5.3% to 990 ppm. The first-stage leaching with HF at 65 °C reduced the ash content to 1.37% by mainly removing Al and Si-containing minerals and subsequent leaching by ferric ions decreased the ash content further (990 ppm) by removing most of the pyrite and fluorides formed during the HF leaching. A two-stage leaching sequence of aqueous HF and  $\text{HNO}_3$  was proposed [141] for coal demineralization. The chemical treatment of a high-volatile bituminous coal with 25% HF for 8 h at 60 °C followed by 25%  $\text{HNO}_3$  for 16 h at 60 °C reduced the ash content from 6.2% to 2.2% and then to 0.3%, respectively. The effect of hydrothermal leaching using solutions of sodium hydroxide and nitric acid has been reported [142].  $\text{HNO}_3$  was more effective than NaOH in reducing elemental concentrations of Mg, Al, Si, S, Mn, Fe, Ca, etc., except V and Ga.

In a chemical cleaning process (the Meyers process, Fig. 3), crushed coal was leached with an acidic solution of ferric sulfate at 100–130 °C for several hours [27]. It removed almost all pyritic sulfur.

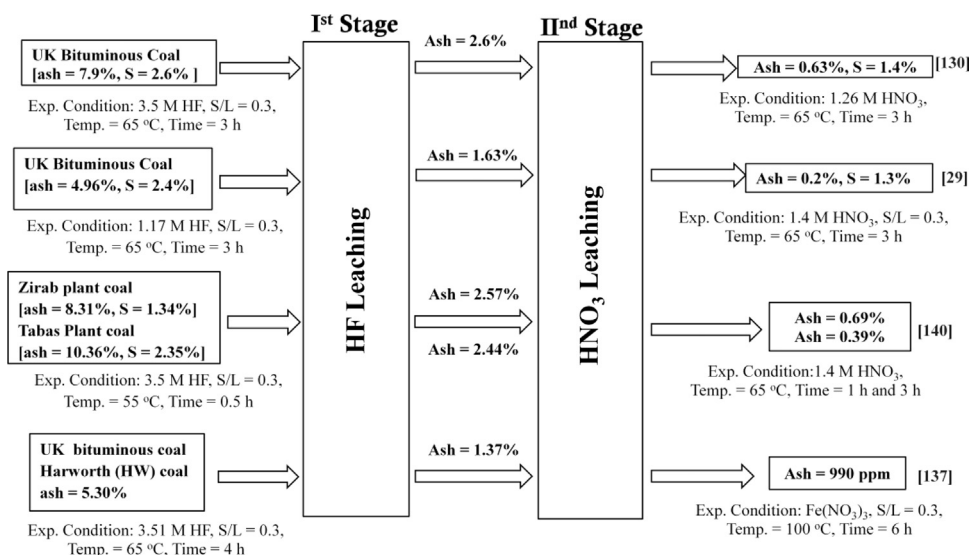
Rodriguez et al. [123] concluded that nitric acid leaching of Spanish coal at atmospheric pressure is effective for desulfurization of intermediate-rank coal, especially for inorganic sulfur removal. In another study [143], it was found that most of the sulfur reduction takes place during the first 5 min. By leaching with 30% nitric acid at 90 °C, the total sulfur content (inorganic sulfur drops down close to zero, reduction in sulfate sulfur 86%, pyritic sulfur 94%, organic sulfur 28.9% after 5 min and 39.1% after 2 h) was quite below the initial organic sulfur content (8.34%). Alvarez et al. [19] observed that  $\text{HNO}_3$  led to a rapid reduction of pyritic and sulfate sulfur. However, FT-IR results of coals leached at high temperatures by nitric acid showed that the oxidation capacity of coal increased and the  $\text{O}^{2-}$  of nitrate group appeared as carbonyl group in molecular structure of coal. Nitrogen substitutes the two adjacent nonbonding hydrogen atoms and nitrates the coal as aromatic nitrogen. For this reason the leaching process with nitric acid is avoided to preserve desirable characteristics and appearance of coal.

Steel et al. [144] investigated the leaching behavior of the mineral matter in coal towards aqueous HCl and HF. HCl was found to dissolve simple compounds such as phosphates and carbonates, but it could not completely dissolve the clays. HF reacts with almost every mineral matter except pyrite. Desulfurization of Tabas Mezino coal was conducted with two consecutive steps of froth flotation at ambient temperature followed by leaching with nitric acid [121]. After these processes total sulfur and ash level were brought down by 75.4% and 53.2% from 1.76% and 16.80% of the raw coal from Mezino coal mines in Tabas, Iran.

Mineral acids for demineralization of coal can modify the surface morphology and harm carbon while reducing the calorific value and creating environmental problems due to their strong oxidizing power. Therefore, some mild leachants were considered for deashing of coal, to avoid above disadvantages [136]. EDTA and citric acid were found as effective as mineral acids like HCl,  $\text{HNO}_3$  and HF. The use of cheap and weak acids such as pyrolygneous acid and citric acid for the generation of ultra-clean coal has proven

**Table 8**  
Chemical beneficiation of some coal samples.

Ash type	Coal type, origin (% ash, % S)	Leaching conditions	% Deashing/desulfurization	Reference
High ash coal	Bituminous coal, Turkey, (44–69% ash, 0.21–0.73% S)	140–500 $\mu\text{m}$ , 0.5 N NaOH – 10% HCl, [S/L: 1/16, 20 min]	46.8% Demineralization.	[133]
	Coking (33.6% ash) and thermal coal (43% ash) Jharkhand, India.	125–250 $\mu\text{m}$ , 20% NaOH – 10% $\text{H}_2\text{SO}_4$ [S/L: 3:50, 24 h]	75–80% Demineralization.	[131]
	Coking coal, Nigeria (32.5% ash)	$\pm 250 \mu\text{m}$ , $\text{H}_2\text{O}$ – $\text{Na}_2\text{CO}_3$ – $\text{H}_2\text{O}$ [90 °C, 25 min]	38.9% Deashing, 19.9% final ash.	[119]
Medium ash coal	Sub-bituminous coal, Iran (16.8% ash, 1.76% S)	30% HCl/ $\text{HNO}_3$ [90 °C, 90 min]	53.2%/75.4% De-ashing/de-sulfurization.	[121]
	Sub-bituminous coal, Italy (15% ash, ~7% S)	< 5 mm, stage I-KOH [S/L:2/5, 95 °C, 6 h], stage II – 3.5% $\text{H}_2\text{O}_2$ [S/L: 2:5, 90 °C, 6 h]	Loss of calorific value with KOH, 12% ash and 4% S.	[134]
	Sub-bituminous HV coal, Thailand (14.7% ash, 4.2% S)	500–1000 $\mu\text{m}$ , 2% methanol and 0.025 g KOH/g coal [S/L: 2:3, 150 °C, 1 h]	58% S and 24% ash removal.	[135]
	Low grade coal, Pakistan (14% ash, 3% S)	250–212 $\mu\text{m}$ , EDTA, citric acid, HCl, $\text{HNO}_3$ and mixed acid: $\text{H}_2\text{O}$ , $\text{HNO}_3$ , HCl and HF (10:5:1:1) [S/L: 1:10, 50 °C, 5 h]	64–71% Deashing by acids and acid mix, 64% de-ashing by EDTA and citric acid.	[136]
Low ash coal	Coking coal, Assam, India (6.60% ash)	212–600 $\mu\text{m}$ , 500 g/L NaOH [S/L: 1/10, 120 °C, 2 h]	~70% Demineralization.	[114]
	Bituminous coal, UK (5.30% ash)	< 52 $\mu\text{m}$ , Stage I: 3.51 M HF [S/L: 3/10, 65 °C, 4 h], Stage II: $\text{Fe}(\text{NO}_3)_3$ [S/L:1:10, 100 °C, 6 h]	Stage I: 1.37% ash Stage II: 990 ppm ash.	[137]
	Victorian brown coal for gas turbine [A: 1.65% ash, 0.5% S; B: 2.35% ash, 0.8% S]	106–150 $\mu\text{m}$ , 1 M pyrolygneous and citric acid and 0.1 M Na-EDTA [S/L:1:10, 24 h]; 1 M ammonium acetate-1–5 M $\text{HNO}_3$ [24h]	Ultra-clean coal by using cheap and weak acids.	[138]



**Fig. 2.** Two-stage leaching of various bituminous coals.

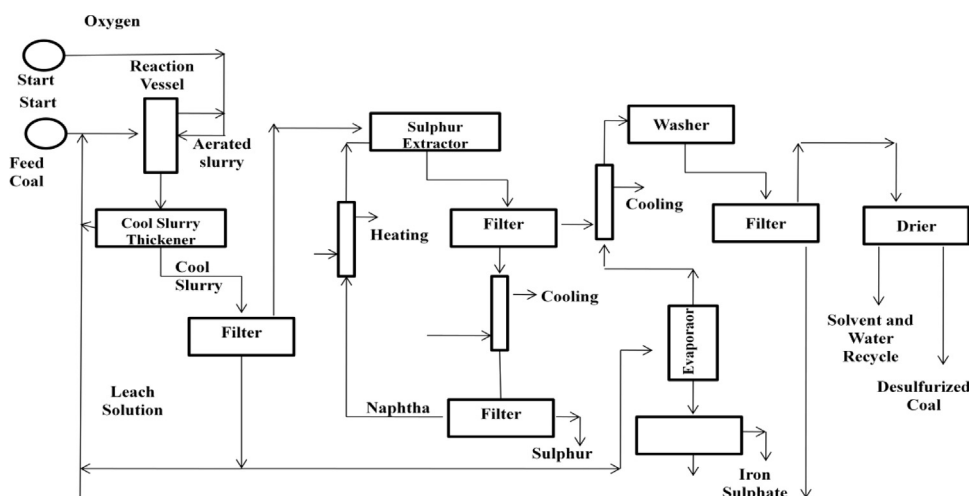
efficiency [138]. Compared to ammonium acetate, these acids can even act as chelating agents to mobilize the nitric acid-insoluble oxides/hydroxides in coal, which in turn can substantially reduce the ash and even sulfur/chlorine contents. The effect of demineralization on an Indian bituminous coal containing 8.20% ash has been studied by leaching using different organic acids viz. acetic, oxalic, citric acid and gluconic, and EDTA at room temperature [145]. When leaching was carried out with citric acid and EDTA, the ash content was reduced to less than 1.94% and 1.81 wt%, respectively. EDTA, acetic acid and gluconic acid leaching was able to remove calcium completely with substantial removal of aluminum and silica, whereas citric acid leaching could remove aluminum completely from the coal matrix. The calorific value of the leached coal reported an increase of 12% with EDTA and gluconic acid leaching.

Leaching of various metals from coal into aqueous solutions containing an acid or a chelating agent was investigated by Ohki et al. [146]. The tendency of metal in coal to leach was roughly divided into three categories, such as largely leached (Ca, Mg and Mn), moderately leached (Cu, Fe, Pb and Zn), and a little leached

(Al, Co, Cr and Ni). Demineralization was found to increase with the increase in  $\text{HNO}_3$  or EDTA concentration. Interestingly even a low concentration of EDTA (0.1 mM) had a considerable ability of leaching of metal like Mn.

The effect of hydrogen peroxide alone and in the presence of dilute sulfuric acid on the desulfurization and demineralization of coal of north-eastern region, India was investigated by Mukherjee et al. [147]. Hydrogen peroxide (15%) alone removed over 76% pyritic sulfur, 70% sulfate sulfur, 5% organic sulfur and over 14% ash at 25 °C, which improved to almost complete removal of pyritic and sulfate sulfur, over 26% organic sulfur and 43% ash in the presence of 0.1 N  $\text{H}_2\text{SO}_4$ . Sulfuric acid acts as catalyst for bringing oxygen and pyrite molecules close to each other which helps in desulfurization. The kinetic and energetic studies using the mixture of 0.1 N  $\text{H}_2\text{SO}_4$  and hydrogen peroxide on desulfurization of Indian coal were reported by Mukherjee and Srivastava [148]. Pyritic sulfur to the tune of about 93% in Baragolai coal and 98% in Ledo coal was removed using a mixture of 15% (v/v) hydrogen peroxide and 0.1 N sulfuric acid. The untreated Baragolai and Ledo coal had pyritic sulfur content of 0.64% and 0.52%, respectively.





Molten caustic leaching (MCL) is another effective process for reducing significant amounts of ash-forming minerals, pyritic sulfur and organic sulfur from solid fossil fuels. Removal of inorganic components from fuel by MCL at 200–400 °C can be

The use of calcium oxide instead of sodium hydroxide was attempted as a leaching agent for the Australian coal [120,161]. Lime ( $\text{Ca}(\text{OH})_2$ ) is efficient and cost effective when compared with

NaOH. Other advantages of using lime instead of sodium hydroxide are (1) less extensive extraction of coal organic matter into the leaching solution; (2) less corrosive to the reactor and equipment materials, and (3) a lesser fouling effect of the residue if chemically treated coal is employed in combustion or gasification applications. Wang and Tomita [161] investigated the chemistry of hydrothermal reactions of  $\text{Ca}(\text{OH})_2$  with pure quartz and pure kaolinite. Wang et al. [120] reported about 76% of ash removal from Newstan coal of Australia by leaching with 5% CaO at 340 °C for 120 min, followed by hydrochloric acid wash; the ash content decreased from 9.2% to 2.2%. Stambaugh et al. [162] and Stambaugh [163,164] used a mixture of 10% NaOH and 2–3%  $\text{Ca}(\text{OH})_2$  as a leaching agent. The process needed fairly rigorous leaching conditions such as, temperature of 250–300 °C and pressure of 3.9–8.4 MPa. The calcium added acts as a sulfur scavenger when the treated coal is burnt.

Recently, the response of Nigerian coal to de-ashing with  $\text{Na}_2\text{CO}_3$ , a cheaper alternative to sodium hydroxide was investigated [119] with an average ash reduction of 38.66% from a feed of 32.55% ash to 19.90% ash. A complete removal of inorganic sulfur and ~70% reduction, in organic sulfur of coal, was achieved with dilute solution of  $\text{Na}_2\text{CO}_3$  at temperature between 120 and 150 °C [165]. Norton et al. [166] reported the removal of 60–90% ash and sulfur from bituminous coals from New Zealand using fused caustic. Markuszewski et al. [167] treated several bituminous coals (~7–15% ash and ~3–5% S) with molten mixtures of NaOH and KOH at 350–370 °C and were able to remove 80–90% ash and 70–80% of total sulfur. In the TRW Gravimelt process a mixture of NaOH and KOH rather than NaOH alone desulfurized coal effectively (> 90% total sulfur) at 350 °C [168].

#### 4.3. Leaching of coal with alkali followed by acid

The alkali leaching of coal in combination with acid washing has been extensively investigated. The advantage of using the leaching agents like NaOH and KOH lies in its applicability for effective removal of most of the minerals from the coals. The dominant phases such as kaolinite and quartz in coal are converted to hydrated alkali-bearing silicate and alumina-silicate complexes (e.g., sodalite), and a portion of pyrite and organic sulfur can also be removed. The products formed from alkali treatment are weakly soluble and hence essentially needs treatment by dilute acid.

Yang et al. [169] reported the demineralization of different coals with three stage leaching involving caustic treatment, followed by sulfuric and nitric acid treatment. In this process, pyrite reacts with NaOH and forms  $\text{Fe}_2\text{O}_3$  and  $\text{Na}_2\text{S}$ . Reactions with NaOH lower the aluminum and silicon contents. Soluble sodium silicates and aluminates are the main products. Dilute sulfuric acid dissolves all of the sodium salts and remaining iron compounds are dissolved by nitric acid. The coal obtained by this process meets the purity (ash  $\leq 0.5\%$ , iron  $\leq 0.03\%$  and silicon  $\leq 0.02\%$ ) requirements of Hall Cell anode grade carbon. The caustic wash was applied to two different lignites from Turkey [113]. At high temperature (187 °C) ~90% of the mineral matter was removed by washing with caustic solution (4 M NaOH) for 60 min followed by acid washing with 1 M HCl at boiling condition for 10 min for both low ash (7%) and high ash (35.6%) coals. The caustic-HF leaching method has been found to be the most effective method for coal deashing, followed by caustic-HCl- $\text{HNO}_3$  and caustic-HCl- $\text{H}_2\text{SO}_4$  leaching methods [115].

The effect of leaching asphaltite samples from Turkey with the molten NaOH method followed by mild acid leaching was investigated by Duz et al. [170]. The complete removal of pyritic sulfur, 70% organic sulfur and ash and 70–79% volatile matter from asphaltites were reported with alkali at a 1:1 ratio with asphaltite at 400 °C for 45 min

followed by wash with 1 M HCl. Ash content was reduced from 18.3% to 6.8% from a coal of Hazro fields, Turkey and 70% of combustible was recovered with the MCL process [171].

Study by Mukherjee and Borthakur [116] showed the removal of 43–50% ash, total inorganic sulfur and ~10% organic sulfur from two Assam coals (8.4% and 10.4% ash, total sulfur 4.3% respectively) by treatment with 16% NaOH solution followed by 10% HCl at 90–95 °C. Subsequent study was reported with KOH alone at 95 °C and 150 °C and in combination with mild acid treatment [118]. At 150 °C, successive treatment of coal with 18% KOH and 10% HCl led to 52.7% desulfurization along with removal all of inorganic sulfur and 37% organic sulfur. Deashing of Assam coking coal from Triop region (Table 8) by sodium hydroxide leaching was studied by Kumar and Gupta [114]. The coal treated at 120 °C with 500 g/L NaOH showed ~70% demineralization from a level of 6.6% ash in the as-received coal.

Reduction in the ash content of physically beneficiated Indian coals by treatment with caustic solution followed by acid washing was reported [14]. Degree of demineralization improved by increasing the reaction time, alkali concentration and temperature, and by reducing the coal particle size. A marginal reduction in sulfur content and significant reduction in phosphorous content was observed after the acid treatment.

A process of chemical cleaning of coal by alkali-acid leaching under mild and ambient pressure was developed by Nabeel et al. [131]. Chemical demineralization of low-grade coal in a three step process, using 1% or 5% aqueous NaOH treatment followed by 1% or 5%  $\text{H}_2\text{SO}_4$  leaching, has been developed with a removal of more than 75–80% of mineral matter. At CSIRO, Australia, a process has been developed [172] for removal of 90% mineral matter from bituminous coal using 10% NaOH at 200–300 °C under pressure followed by acid treatment.

The effect of aqueous caustic and various acid treatments on the removal of mineral matter in asphaltite was investigated by Doymaz et al. [173]. About 59.6% of the mineral matter could be removed by 10%  $\text{H}_2\text{SO}_4$  and 40% HF after pre-treating the coal with 5% NaOH solution. Similarly, Bolat et al. [133] studied the chemical demineralization of Turkish coal using different acids (HF, HCl,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ ) alone and in combination of 0.5 N aqueous NaOH with one or two acids and found maximum of 46.78% demineralization. In another study a low level of 3.3% ash content was obtained from the Tuncbilek lignite when treated with 30% NaOH and 10% HCl [26]. Baruah and Khare [174] reported the removal of inorganic and organic sulfur, and minerals by solvent extraction and alkali treatment of the coal oxidized by  $\text{H}_2\text{O}_2$ - $\text{HCOOH}$ . Chemical leaching of the two high sulfur coal named as Ledo and Baragorai from Assam, India with the ash content of 10.35% and 5.70%, and total sulfur content of 3.57% and 5.30%, respectively, was investigated by Baruah et al. [175]. The aqueous leaching removed 89.7% and 77.05% sulfur in 120 h and 45 °C in Ledo and Baragorai coals, respectively.

## 5. Conclusion

For the demineralization of coal, physical processes are the most economical methods and are used commercially. Generally the gravity based processes are quite useful for deashing of coal of larger size particles (> 0.5 mm). Processes based on surface properties of coal like froth flotation are also quite successful for the particles below 0.5 mm size, but has the problem of utilizing large quantity of water and results in generation of tailings and increase in moisture content as well. Whenever fine size particles from crushing/grinding are needed to liberate product from the gangue, dry fluidization could be an alternative to the wet chemical flotation and cost-effective as well.

Though the mineral-rich grains may be removed by physical beneficiation, but for finely dispersed minerals bound to the coal structure or organic bound elements chemical beneficiation is an effective method. However, these methods are expensive due to the requirements of chemical reagents and dewatering of the fine-sized slurry. Almost all studies on the demineralization of coal have ignored the recyclability of wastewater generated and its treatment as presently none of these methods are used industrially. As regards the bio-desulfurization of coal complete development using native microbes is yet to emerge, although desulfurization of inorganic as well as organic sulfur can be achieved. Establishing the bio-desulfurization process on pilot/large scale may ensure its exploitation for the coal preparation.

For general applications like thermal power generation, cement and non-critical metallurgical industries, chemical beneficiation methods may not compete with the physical cleaning technologies presently followed for the coal preparation. This is because beneficiation methods need to have low cost and must be environmental friendly. However, the use of chemical methods in a hybrid approach with the physical method as a pre-treatment step appears to be an attractive option. The combined physical and chemical cleaning has shown the potential for deashing and demineralization of various coals. By the combined physical–chemical beneficiation process the cleaner and ultra-clean coals can be produced for specific use like metallurgical and gas turbine applications.

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## References

- [1] Singh R, Sinha SN. Beneficiation of high ash Indian coal-problems and prospects. *Indian Min Eng J* 2003;1–4.
- [2] BP (British Petroleum) statistical review of world energy. London; June 2014.
- [3] Garg P. Energy scenario and vision 2020 in India. *J Sustain Energy Environ* 2012;3:7–17.
- [4] Dwari RK, Rao KH. Tribo-electrostatic behavior of high ash non-coking Indian thermal coal. *Int J Miner Process* 2006;81(2):93–104.
- [5] Coal Marketing International Ltd.; 2012. URL <<http://www.coalmarketinginfo.com/advanced-coal-science>>.
- [6] Haldar DD. Beneficiation of non-coking coals: basic concepts and technology routes. In: Singh R, Das A, Banerjee PK, Bhattacharya KK, Goswami NG, editors. *Proceedings of the XI International Seminar on Mineral Processing Technology (MPT-2010)*. Jamshedpur: Allied publishers; 2010. p. 419–27.
- [7] Ward CR. Analysis and significance of mineral matter in coal seams. *Int J Coal Geol* 2002;50:135–68.
- [8] IEA Report. Coal in the Energy Supply of India. International Energy Agency–Coal Industry Advisory Board. India; 2002.
- [9] ASTM, 1998: Annual Book of American Society for Testing and Materials Standards, Chapter D 388–98; p. 174–99.
- [10] Valković V. Trace elements in coal, vol. I. Boca Raton, Fla.: CRC Press; 1983.
- [11] BP (British Petroleum) Statistical Review of World Energy. URL <[bp.com/statisticalreview](http://bp.com/statisticalreview)>; June 2012.
- [12] Indian Minerals Year Book (IMYB). Part II, Coal & Lignite. 50th ed. Government of India, Ministry of Mines, Indian Bureau of Mines; 2011.
- [13] Coal Directory of India. Coal Controller's Organisation, Kolkata; 2010–11.
- [14] Dash PS, Kumar SS, Banerjee PK, Ganguly S. Chemical leaching of high ash Indian coals for production of low ash clean coal. *Miner Process Extract Metall Rev* 2013;34:223–39.
- [15] CPCB. Thermal power plants – environmental regulation. P.C.I. Division. India: Central Pollution Control Board; 1997.
- [16] Karaca S, Akyurek M, Bayrakceken S. The removal of pyritic sulfur from Askale lignite in aqueous suspension by nitric acid. *Fuel Process Technol* 2003;80:1–8.
- [17] Ahnokitpanit E, Prasassarakich P. Coal desulfurization in aqueous hydrogen peroxide. *Fuel* 1989;68:819–24.
- [18] Aitani AM, Ali MF, Al-Ali HH. Review of non-conventional methods for the desulfurization of residual fuel oil. *Pet Sci Technol* 2000;18(5):537–53.
- [19] Alvarez R, Clemente C, Gomez-Limon D. The influence of nitric acid oxidation of low rank coal and its impact on coal structure. *Fuel* 2003;82:2007–15.
- [20] Babich JA, Mouljin JA. Science and technology of novel processes for deep desulfurization of oil refinery streams – a review. *Fuel* 2003;82:607–31.
- [21] Charutawai K, Ngamprasertsith S, Prasassarakich P. Supercritical desulfurization of low rank coal with ethanol/KOH. *Fuel Process Technol* 2003;84:207–16.
- [22] Demirbas A, Balat M. Coal desulfurization via different methods. *Energy Sources* 2004;26:541–50.
- [23] Karaca H, Ceylan K. Chemical cleaning of Turkish lignites by leaching with aqueous hydrogen peroxide. *Fuel Process Technol* 1997;50:19–33.
- [24] Karaca H, Ceylan K, Olcay A. Catalytic dissolution of two Turkish lignites in tetralin under nitrogen atmosphere: effects of the extraction parameters on the conversion. *Fuel* 2001;80:559–64.
- [25] Karaca H, Onal Y. Demineralization of lignites by single and successive pretreatment. *Fuel* 2003;82(12):1517–22.
- [26] Karaca H, Yildiz Z. Desulfurization of fuel by leaching using H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>. *Pet Sci Technol* 2005;23(3–4):285–98.
- [27] Meyers RA. Coal desulphurization. New York: Marcel Dekker, Inc.; 1977.
- [28] Ozbas KE, Hicilylmaz C, Kok MV. The effect of lime addition on the combustion properties and sulfur contents of three different coals. *Energy Source* 2002;24:643–52.
- [29] Steel KM, Patrick JW. The production of ultra-clean coal by sequential leaching with HF followed by HNO<sub>3</sub>. *Fuel* 2003;82:1917–20.
- [30] Yildiz Z, Karaca H. Determination of optimum process parameters in desulfurization of fuel oil. *Pet Sci Technol* 2005;23:371–84.
- [31] Akers D, Dospoy R. Role of coal cleaning in control of coal toxics. *Fuel Process Technol* 1994;39(1–3):73–86.
- [32] Palmer S, Hippo E, Dorai X. Selective oxidation pre-treatments for the enhanced desulfurization of coal. *Fuel* 1995;74:193–200.
- [33] Honaker RQ, Paul BC, Wang D, Ho K. Enhanced gravity separation: an alternative to flotation. In: Kawatra SK, editor. *Proceedings of high efficiency coal preparation: an international symposium*. Colorado: SME Inc.; 1995. p. 70–8.
- [34] Honaker RQ, Singh N, Govindarajan B. Application of dense-medium in an enhanced gravity separator for fine coal cleaning. *Miner Eng* 2000;13(4):415–27.
- [35] Özgen S, Malkoç Ö, Doğancık C, Sabah E, Şapçı FO. Optimization of a multi gravity separator to produce clean coal from Turkish lignite fine coal tailings. *Fuel* 2011;90(4):1549–55.
- [36] Oruç F, Özgen S, Sabah E. An enhanced-gravity method to recover ultra-fine coal from tailings: Falcon concentrator. *Fuel* 2010;89:2433–7.
- [37] Honaker RQ, Wang D, Ho K. Application of the Falcon concentrator for fine coal cleaning. *Miner Eng* 1996;9(11):1143–56.
- [38] Rath RK, Singh R, Bhattacharya KK. Processing of coal waste by enhanced gravity separation and froth flotation. In: *Proceedings of international conference on coal and coke*. National Metallurgical Laboratory, Jamshedpur; 2011.
- [39] Das A, Sarkar B, Ari V, Roy S. Efficient recovery of combustibles from coking coal fines. *Miner Process Extract Metall Rev* 2010;31:236–49.
- [40] Couch GR. Advanced coal cleaning technology, IEA Coal Research. IEA Coal Research Publishers; 1991.
- [41] Özgen S, Türksöy VO, Sabah E, Oruç F. Process development studies on recovery of clean coal from ultra fine hard coal tailings using enhanced gravity separator. *Can J Chem Eng* 2009;87:715–25.
- [42] Demirbas A. Demineralization and desulfurization of coals via column froth flotation and different methods. *Energy Convers Manag* 2002;43:885–95.
- [43] Budge G. RJB refines treatments at Gascoigne Wood. *Mine Quarry* 1998;48–52.
- [44] Yoon RH, Luttrell GH, Adel GT, Mankosa MJ. The application of Microcell column flotation to fine coal cleaning. In: *Proceedings of engineering foundation conference on fine coal cleaning*. Palm Coast, FL; 1990.
- [45] Mohanty MK, Honaker RQ. Performance optimization of Jameson flotation technology for fine coal cleaning. *Miner Eng* 1999;12(4):367–81.
- [46] Firth B. Turbo flotation: faster, cleaner, cheaper fine coal recovery. *The Australian Coal Review*; 1999.
- [47] Atesok G, Boylu F, Celik MS. Carrier flotation for desulfurization and deashing of difficult-to-float coals. *Miner Eng* 2001;14(6):661–70.
- [48] Jena MS, Biswal SK, Rudramuniyappa MV. Study on flotation characteristics of oxidized Indian high ash sub-bituminous coal. *Int J Miner Process* 2008;87:42–50.
- [49] Ayhan FD, Abakay H, Saydut A. Desulfurization and deashing of Hazro coal via a flotation method. *Energy Fuels* 2005;19:1003–7.
- [50] Groppo JG, Parekh BK. Continuous pilot-scale testing of column flotation for recovery of fine. *Miner Eng* 1990;42(10):1189–92.
- [51] Cilek EC, Aktas H, Sari A. Desulfurization of Turkish lignites by column flotation. *Energy Educ Sci Technol* 2000;5:93–103.
- [52] Erol M, Cigdem C, Zeki A. The effect of reagents and reagent mixtures on froth flotation of coal fines. *Int J Miner Process* 2003;71:131–45.
- [53] Reza EM, Farahnaz E. Reduction of sulfur and ash from Tabas coal by froth flotation. *Iran J Chem Eng* 2007;26(2):35–40.
- [54] Xiu-Xiang T, Cao YJ, Liu J, Shi KY, Liu JY, Maoming F. Studies on characteristics and flotation of a hard-to-float high-ash fine coal. *Proced Earth Planet Sci* 2009;1:799–806.
- [55] Reddy PSR, Kumar SG, Bhattacharya KK, Sastri SRS, Narasimhan KS. Flotation column for fine coal beneficiation. *Int J Miner Process* 1988;24(2):161–72.
- [56] Sastri SRS. Recovery of coal fines using column flotation. *Miner Eng* 1988;1(4):359–63.



- [57] Reddy PSR, Biswal SK, Prakash S, Bhaumik SK, Sastri SRS. Recovery of coal fines from rejects by column flotation. In: Bhattacharyya P, Singh R, Goswami NG, editors. Processing of Fines, 2. Jamshedpur, India: NML; 2000. p. 213–21.
- [58] Tsai SC. Coal Science and technology 2: Fundamentals of coal beneficiation and utilization. Amsterdam: Elsevier Scientific Publishers; 1982.
- [59] Baruah MK, Kotoky P, Baruah J, Bora GC. Cleaning of Indian coals by agglomeration with xylene and hexane. Sep Purif Technol 2000;20:235–41.
- [60] Malik A, Singh DP, Sharma S, Dastidar MG, Roychoudhury PK. Oil agglomeration for recovery of coal fines: effect of vegetable oil and bacterial pretreatment. Coal Prep 1999;20:247–68.
- [61] Aktaş Z. Some factors affecting spherical oil agglomeration performance of coal fines. Int J Miner Process 2002;65:177–90.
- [62] Ergun S, Bean EE. Magnetic separation of pyrite from coals. (Report of Investigation No. 7181). Pittsburgh: U.S. Bureau of Mines; 1968.
- [63] Liu YA, Lin CJ. Assessment of sulfur and ash removal from coals by magnetic separation. IEEE Trans Magn 1976;12:538–50.
- [64] Zhou S, Garbett ES, Boucher RF. Gravity-enhanced magnetic (HGMS) coal cleaning. Ind Eng Chem Res 1996;35:4257–63.
- [65] Atesok G, Perek KT, Dincer H, Celik MS. Reduction of ash and sulfur contents of low-rank Turkish semicoking lignite by high intensity dry magnetic separation. Coal Prep 1999;20:179–90.
- [66] Kelly EG, Spottiswood DJ. The theory of electrostatic separations: a review Part I. fundamentals. Miner Eng 1989;2(1):33–46.
- [67] Mazumder MK, Tennal KB, Lindquist D. Electrostatic beneficiation of coal. In: Proceeding of the 10th annual coal preparation, utilization and environmental control contractors conference; 1994. p. 111–6.
- [68] Lockhart NC. Review paper. Beneficiation of coal. Powder Technol 1984;40:17–42.
- [69] Carta M, Del FC, Ciccu R, Curreli L, Agus M. Technical and economical problems connected with the dry cleaning of raw coal and in particular with pyrite removal by means of electric separation. In: Partridge A, editor. Proceedings of 7th International Coal Preparation Congress. Australia: Adept Printing Pvt. Ltd; 1976. p. 1–35.
- [70] Alfano G, Carhini P, Ciccu R, Ghiani M, Peretti R, Zucca A. Progress in triboelectric separation of minerals. In: Forssberg E, editor. Proceedings of XVI International Mineral Processing Congress. Amsterdam: Elsevier Pub BV; 1988. p. 833–44.
- [71] Anderson JM, Parobek L, Bergougnou MA, Inculet II. Electrostatic separation of coal macerals. IEEE Trans Indust Appl, 1A-15 1979;3:291–3.
- [72] Mukherjee A, Gidaspow D, Wasan DT. Surface charge of Illinois coal and pyrites for dry electrostatic cleaning. In: Preprints of Papers-American Chemical Society, Division of Fuel Chemistry 1987;32(1):395–407.
- [73] Schaefer JL, Ban H, Stencel JM. Non-intrusive measurement of particle charge relating to electrostatic dry coal cleaning. In: Proceeding of international Pittsburgh coal conference. PA, USA; 1992. p. 259–64.
- [74] Schaefer JL, Ban H, Stencel JM. Triboelectrostatic dry coal cleaning. In: Proceedings of international Pittsburgh coal conference. PA, USA, vol. 1; 1994. p. 624–9.
- [75] Ban H, Schaefer JL, Stencel JM. Particle tribocharging characteristics relating to electrostatic dry coal cleaning. Fuel 1994;73:1108–15.
- [76] Hower JC, Hang B, Schaefer JL, Stencel JM. Maceral/microlitho type partitioning through triboelectrostatic dry coal cleaning. Int J Coal Geol 1997;34:277–86.
- [77] Soong Y, Link TA, Schoffstall MR, Gray ML, Fauth DJ, Knoer JP, et al. Dry beneficiation of Slovakian coal. Fuel Process Technol 2001;72(3):185–98.
- [78] Inculet II, Quingley RM, Bergougnou MA, Brown JD. Electrostatic beneficiation of hat creek coal in the fluidized state. CIM Bull 1980:51–61.
- [79] Dwari RK, Hanumantha Rao K. Tribo-electrostatic behavior of high ash non-coking Indian thermal coal. Int J Miner Process 2006;81:93–104.
- [80] Zhang X, Duan DY, Tian B, Wang JS, Deng F, Li HS, et al. Research on the tribo-electrostatic separation of minerals from coal. Proced Earth Planet Sci 2009;1(1):845–50.
- [81] Marland S, Merchant A, Rowson N. Dielectric properties of coal. Fuel 2001;80:1839–49.
- [82] Jones DA, Lelyveld TP, Mavrofidis SD, Kingman SW, Miles NJ. Microwave heating applications in environmental engineering – a review. Resour Conserv Recycl 2002;34:75–90.
- [83] Church RH, Webb WE, Salsman JB. Dielectric properties of low loss materials. Washington, US: US Bureau of Mines Report of Investigations 9194; 1993.
- [84] Harrison PC, Rowson NA. The use of dielectric heating to alter mineral properties. Icheme research event. In: Proceedings of the second European conference for young researchers. Leeds, England; 1996.
- [85] Chatterjee I, Misra M. Electromagnetic and thermal modeling of microwave drying of fine coal. Miner Metall Process 1991:110–4.
- [86] Shuey RT. Semiconductor ore minerals (developments in economic geology 4). Amsterdam: Elsevier; 1976.
- [87] Maxwell E, Kelland DR, Jacobs IS, Levinson LM. Magnetic separation and thermo-magneto-chemical properties of coal liquefaction mineral particulates. Fuel 1982;61:369–76.
- [88] Weng SH. Mossbauer analysis of the microwave desulfurization process of raw coal. J Appl Phys 1993;73:4680–2.
- [89] Zavitsanos PD, Golden JA. Tracking pyritic sulfur in the microwave desulphurisation of coal. J Appl Phys 1982;53:2730–2.
- [90] Rowson NA, Rice NM. Desulphurisation of coal using low power microwave energy. Miner Eng 1990;3(3–4):363–8.
- [91] Zavitsanos PD, Bleiler KW. Coal desulfurization induces thermo-chemical, in situ reactions between sulfur and other elements in coal, US Patent 4076607; 1978.
- [92] Uslu T, Atalay Ü. Microwave heating of coal for enhanced magnetic removal of pyrite. Fuel Process Technol 2003;85:21–9.
- [93] Haque KE. Microwave energy for mineral treatment processes – a brief review. Int J Miner Process 1999;57:1–24.
- [94] Bykov YV, Rybakov KI, Semenov VE. High-temperature microwave processing of materials. J Phys D: Appl Phys 2000;34:55–75.
- [95] Andrés JM, Ferrando AC, Membrado L. Chemical desulfurization of coal with hydroiodic acid. Energy Fuels 1996;10:425–30.
- [96] Yürüm Y, Elsamak GG, Oztas NA. Chemical desulphurisation of Turkish Cayirhan lignite with HI using microwave and thermal energy. Fuel 2002;82:531–7.
- [97] Hayashi J, Oku K, Kusakabe K, Morooka S. The role of microwave irradiation in coal desulphurisation with molten caustics. Fuel 1990;69:739–42.
- [98] Jorjani E, Rezaei B, Vossoughi M, Osanloo M. Desulphurisation of Tabas coal with microwave irradiation/peroxyacetic acid washing at 25, 55 and 85 °C. Fuel 2003;83:943–9.
- [99] Van Houwelingen JA, De Jong TPR. Dry cleaning of coal: review, fundamentals and opportunities. Geol Belg 2004;7(3–4):335–43.
- [100] Manoj B, Elcey CD. Demineralization of coal by stepwise bioleaching: a study of sub-bituminous Indian coal by FTIR and SEM. J Univ Chem Technol Metall 2010;45(4):385–90.
- [101] Silverman MP, Rogoff MH, Wender I. Removal of pyritic sulfur from coal by bacterial action. Fuel 1963;42:113–24.
- [102] Dugan PR, Apel WA. Microbiological desulfurization of coal. In: Murr LE, Torma AE, Brierley JA, editors. Metallurgical applications of bacterial leaching and related microbiological phenomena. New York: Academic Press; 1978. p. 223–50.
- [103] Zarubina NN, Lyalikova NN, Shmuk EI. Investigation of microbiological oxidation of coal pyrite. Invest Akad Nank Ssr Otdel Tekh Mauk Me Toplivo 1959;1:117–9.
- [104] Andrews GF, Maczuga J. Bacterial removal of pyrite from coal. Fuel 1984;63:297–302.
- [105] Rawlings DE, Tributsch H, Hansford GS. Reasons why 'Leptospirillum' – like species rather than Thiobacillus ferrooxidans are the dominant iron-oxidizing bacteria in many commercial processes for the biooxidation of pyrite and related ores. Microbiol 1999;145:5–13.
- [106] Harrison AP. The acidophilic thiobacilli and other acidophilic bacteria that share their habitat. J Ann Rev Microbiol 1984;38:265–92.
- [107] Detz D, Barvinchak G. Microbial desulphurisation of coal. Min Congr J 1979;65:75–86.
- [108] Kargi F, Robinson JM. Removal of organic sulfur from bituminous coal use of the thermophilic organism *Sulfolobus acidocaldarius*. Fuel 1986;65:397–9.
- [109] Kargi F, Robinson JM. Microbial desulfurization of coal by the thermophilic microorganism *Sulfolobus acidocaldarius*. Biotechnol Bioeng 1982;24:2115–21.
- [110] Hone HJ, Beyer M, Ebner HG, Klein J, Juntgen H. Microbial desulphurization of coal – development and application of a slurry reactor. Chem Eng Technol 1987;10:173–6.
- [111] Couch GR. Biodesulfurization of coal, IEA coal research report, London; 1993.
- [112] Balaz P, LaCount RB, Kern DG, Turcaniova L. Chemical treatment of coal by grinding and aqueous caustic leaching. Fuel 2001;80:665–71.
- [113] Culfaz M, Ahmed M, Gürkan S. Removal of mineral matter and sulfur from lignites by alkali treatment. Fuel Process Technol 1996;47:99–109.
- [114] Kumar M, Gupta RC. Demineralization study of Indian Assam coking coal by sodium hydroxide leaching. Energy Sources 1997;19:723–30.
- [115] Kumar M, Shankar RH. Removal of ash from Indian Assam coking coal using sodium hydroxide and acid solutions. Energy Sources 2000;22(2):187–96.
- [116] Mukherjee S, Borthakur PC. Chemical demineralization/desulfurization of high sulfur coal using sodium hydroxide and acid solutions. Fuel 2001;80:2037–40.
- [117] Mukherjee S. Demineralization and desulfurization of high-sulfur Assam coal with alkali treatment. Energy Fuels 2003;17:559–64.
- [118] Mukherjee S, Borthakur PC. Effect of leaching high sulfur subbituminous coal by potassium hydroxide and acid on removal of mineral matter and sulfur. Fuel 2003;82:783–8.
- [119] Adeleke AA, Ibitoye SA, Afonja AA, Chagga MM. Multistage caustic leaching de-ashing of Nigerian Lafia-Obi coal. Pet Coal 2011;53(4):259–65.
- [120] Wang J, Zhang ZG, Kobayashi Y, Tomita A. Chemistry of Ca(OH)<sub>2</sub> leaching on mineral matter removal from coal. Energy Fuels 1996;10:386–91.
- [121] Alam HG, Moghaddam AZ, Omidkhan MR. The influence of process parameters on desulfurization of Mezino coal by HNO<sub>3</sub>/HCl leaching. Fuel Process Technol 2009;90:1–7.
- [122] Khan MA, Mohmand MI. Demineralization of Sor-Range Coal with HNO<sub>3</sub> and the determination of trace elements in the acid extracts. J Chem Soc Pak 1990;12(3):263–6.
- [123] Rodriguez RA, Jul CC, Gomez-Limon D. The influence of process parameters on coal desulfurization by nitric leaching. Fuel 1996;75:606–12.
- [124] Paul M, Seferinoglu M, Ayçık GA, Sandström A, Smith ML, Paul J. Acid leaching of ash and coal: time dependence and trace element occurrences. Int J Miner Process 2006;79:27–41.
- [125] Vasilakos NP, Clinton CS. Chemical beneficiation of coal with aqueous hydrogen peroxide/sulphuric acid solutions. Fuel 1984;63(11):1561–3.
- [126] Meyers RA. Hydrocarbon process 1975;54(6):93–6.
- [127] Ali A, Srivastava SK, Haque R. Chemical desulphurization of high sulfur coals. Fuel 1992;71:835–9.



- [128] Li W, Cho EH. Coal desulphurization with sodium hypochlorite. *Energy Fuels* 2005;19:499–507.
- [129] Steel KM, Besida J, O'Donnell TA, Wood DG. Production of ultra-clean coal. Part-III. Effect of coal's carbonaceous matrix on the dissolution of mineral matter using hydrofluoric acid. *Fuel Process Technol* 2002;76:51–9.
- [130] Steel KM, Patrick JW. The production of ultra-clean coal by chemical demineralization. *Fuel* 2001;80:2019–23.
- [131] Nabeel A, Khan TA, Sharma DK. Studies on the production of ultra-clean coal by alkali-acid leaching of low-grade coals. *Energy Sources, Part A: Recov Util Environ Effects* 2009;31:594–601.
- [132] Andres JM, Ferrando AC, Membrado L. Chemical desulfurization of coal with hydroiodic acid. *Energy Fuels* 1996;10:425–30.
- [133] Bolat E, Saglam S, Piskin S. Chemical demineralization of a Turkish high ash bituminous coal. *Fuel Process Technol* 1998;57:93–9.
- [134] Fois E, Pistis A, Melis F, Mura G, Lallai A. Sulfur removal from sulcis coal by sequential leaching with KOH followed by H<sub>2</sub>O<sub>2</sub>. *Chem Eng Trans* 2010;19:61–6.
- [135] Ratanakandilok S, Ngamprasertsith S, Prasassarakich P. Coal desulfurization with methanol/water and methanol/KOH. *Fuel* 2001;80:1937–42.
- [136] Shakerullah M, Ahmad I, Rehman H, Ishaq M, Khan U, Ullah H. Effective chemical leaching and ash depletion of low rank coal with EDTA and citric acid. *J Chem Soc Pak* 2006;28(1):56–61.
- [137] Wu Z, Steel KM. Demineralization of a UK bituminous coal using HF and ferric ions. *Fuel* 2007;86:2194–200.
- [138] Wijaya N, Choo TK, Zhang L. Generation of ultra-clean coal from Victorian brown coal – sequential and single leaching at room temperature to elucidate the elution of individual inorganic elements. *Fuel Process Technol* 2011;92:2127–37.
- [139] Wang J, Tomita A. Removal of mineral matter from some Australian coals by Ca(OH)<sub>2</sub>/HCl leaching. *Fuel* 1998;77(15):1747–53.
- [140] Jorjani E, Ghasemi CH, Tayebi KM. Ultra clean coal production by microwave irradiation pretreatment and sequential leaching with HF followed by HNO<sub>3</sub>. *Fuel Process Technol* 2011;92(10):1898–904.
- [141] Rubiera F, Arenillas A, Arias B, Pis JJ, Suarez-Ruiz I, Steel KM, et al. Combustion behavior of ultra clean coal obtained by chemical demineralization. *Fuel* 2003;82:2145–51.
- [142] Blanchard LJ, Robertson JD, Srikanthapur S, Parekh BK, Huggins FE. Potentially hazardous trace elements in Kentucky coals. *Am Chem Soc, Div Fuel Chem Preprints* 1995;40(4):828–32.
- [143] Rodriguez RA, Jul CC, Gomez-Limon D. Evolution of the organic sulfur and other components during nitric acid leaching of Mequinenza coal. *Fuel* 1997;76:1445–50.
- [144] Steel KM, Besida J, O'Donnell TA, Wood DG. Production of ultra-clean coal. Part-I – dissolution behavior of mineral matter in black coal toward hydrochloric and hydrofluoric acid. *Fuel Process Technol* 2001;70:171–92.
- [145] Manoj B. Chemical demineralization of high volatile Indian bituminous coal by carboxylic acid and characterization of the products by SEM/EDS. *J Environ Res Dev* 2012;6(3A):653–9.
- [146] Ohki A, Nakajima T, Yamashita H, Iwashita A, Takanashi H. Leaching of various metals from coal into aqueous solutions containing an acid or a chelating agent. *Fuel Process Technol* 2004;85:1089–102.
- [147] Mukherjee S, Mahiuddin S, Borthakur PC. Demineralization and desulfurization of subbituminous coal with hydrogen peroxide. *Energy Fuels* 2001;15:1418–24.
- [148] Mukherjee S, Srivastava SK. Kinetics and energetic of high-sulfur north eastern India coal desulfurization using acidic hydrogen peroxide. *Energy Fuels* 2004;18:1764–9.
- [149] Kara H, Ceylan R. Removal of sulfur from four central Anatolian lignites by NaOH. *Fuel* 1988;67:170–2.
- [150] Mazumdar BK, Sengupta AN. De-ashing of coal. *Science Today* 1980; January:42–3.
- [151] Saydut A, Duz MZ, Erdogan S, Tonbul Y, Hamamci C. Chemical leaching on sulfur and mineral matter removal from asphaltite (Harbul, SE Anatolia, Turkey). *Energy Sources, Part A: Recov Util Environ Effects* 2011;33(5):383–91.
- [152] Friedman SJ, Warzinski RP. Chemical cleaning of coal. *Transactions of the American Society of Mechanical Engineers. J Eng Power* 1977;99A:361–4.
- [153] Yaman S, Kucukbayrak S. Sulfur removal from Gediz lignite using aqueous sodium hydroxide solutions under mild oxidative conditions. *Energy Source* 1999;21:829–37.
- [154] Lolja SA. A model for alkaline removal of sulfur from a low-rank coal. *Fuel Process Technol* 1999;60:185–94.
- [155] Chriswell CD, Shah ND, Kaushik SM, Markuszewski R. Chemical cleaning of coal by molten caustic leaching after pretreatment by low-temperature devolatilization. *Fuel Process Technol* 1989;22(1):95–106.
- [156] Chriswell CD, Shah ND, Markuszewski R. Counter current washing of Pittsburgh No. 8 coal after leaching with molten mixture Na and K hydroxides. *Sep Sci Technol* 1991;26(7):961–75.
- [157] Lee SH, Shon EK. Effect of molten caustic leaching on the combustion characteristics of anthracite. *Fuel* 1997;76(3):241–6.
- [158] Araya PE, Ohlbaum RB, Droguett SE. Study of the treatment of sub bituminous coals by NaOH solutions. *Fuel* 1981;60:1127–30.
- [159] Wang ZY, Ohtsuka Y, Tomita A. Removal of mineral matter from coal by alkali treatment. *Fuel Process Technol* 1986;13:279–89.
- [160] Kaushik SM, Norton GA, Markuszewski R. Behavior of ash-forming mineral matter in coal during chemical cleaning with molten caustic. *Preprints of papers, American Chemical Society, Division of Fuel Chemistry, USA* 1988;33(2):18–27.
- [161] Wang J, Tomita A. Hydrothermal reaction of Ca(OH)<sub>2</sub> with quartz in connection with coal demineralization. *Ind Eng Chem Res* 1997;36(5):1464–9.
- [162] Stambaugh EP, Miller JF, Tam SS, Chauhan SP, Feldman HE, Carlton HE, et al. *Hydrocarb Process* 1975;54(7):115–6.
- [163] Stambaugh EP. Extracting sulfur and ash. US Patent 4,055,400; 1977.
- [164] Stambaugh EP. Hydrothermal coal Process. In: Wheelock TD, editors. *American chemical society symposium series*. Washington DC; 1977. p. 198–205.
- [165] Markuszewski R, Chung KC, Wheelock TD. Coal desulphurization by leaching with alkaline solutions containing oxygen. In: Rogers SE, Lemmon AW, editors. *EPA symposium on coal cleaning to achieve energy and environmental goals*, Hollywood FL USA; 1978.
- [166] Norton GA, Mroch DR, Chriswell CD, Markuszewski R. In: Chugh YP, Caudle RD, editors. *Processing and utilization of high sulfur coals – II*. New York: Elsevier; 1987. p. 213–23.
- [167] Markuszewski R, Mroch DR, Norton GA, Straszheim WE. Desulfurization and demineralization of coal by molten NaOH/KOH mixtures. *Preprints paper – American Chemical Society, Division of Fuel Chemistry* 1985;30:41–8.
- [168] Kusakabe K, Orita M, Morooka S, Kato Y, Kusunoki K. Simultaneous desulfurization and demineralization of coal. *Fuel* 1989;68(3):396–9.
- [169] Yang RT, Das SK, Tsai BMC. Coal demineralization using sodium hydroxide and acid solutions. *Fuel* 1985;64:735–42.
- [170] Duz MZ, Erdogan S, Saydut A, Merdivan M, Hamamci C. Effect of molten caustic leaching on demineralization and desulfurization of asphaltite. *Energy Sources, Part A: Recov Util Environ Effects* 2008;30(17):1637–44.
- [171] Duz MZ, Saydut A, Erdogan S, Hamamci C. Removal of sulfur and ash from coal using molten caustic leaching, a case study from Hazro fields, Turkey. *Energy Explor Exploit* 2009;27:391–400.
- [172] Waugh AB, Bouling KG. Removal of mineral matter from bituminous coals by aqueous chemical leaching. *Fuel Process Technol* 1984;9:217–33.
- [173] Doymaz I, Gulen J, Piskin S. The effect of aqueous caustic and various acid treatments on the removal of mineral matter in asphaltite. *Energy Sources, Part A: Recov Util Environ Effects* 2007;29(4):337–46.
- [174] Baruah BP, Khare P. Desulfurization of oxidized Indian coals with solvent extraction and alkali treatment. *Energy Fuels* 2007;21:2156–64.
- [175] Baruah BP, Saikia BK, Kotoky P, Rao PG. Aqueous leaching on high sulfur sub-bituminous coals, in Assam, India. *Energy Fuels* 2006;20:1550–5.